## **Atmospheric Sulphur Dioxide and Sulphate Aerosols: Spatial and Seasonal Variability**

A THESIS

Submitted for the Award of Ph. D degree of

MOHANLAL SUKHADIA UNIVERSITY

In the

**Faculty of Science** 

By

**Timmy Francis** 



Under the Supervision of

PROFESSOR M. M. Sarin SENIOR PROFESSOR

Physical Research Laboratory, Ahmedabad - 380 009, India.

# DEPARTMENT OF CHEMISTRY MOHANLAL SUKHADIA UNIVERSITY UDAIPUR

2011

# **DECLARATION**

I, **Mr. Timmy Francis**, S/o Mr. Francis. C. A, resident of B-301, Samarthya Residency, D-Cabin, Ahmedabad – 380019, hereby declare that the research work incorporated in the present thesis entitled "*Atmospheric Sulphur Dioxide and Sulphate Aerosols: Spatial and Seasonal Variability*" is my own work and is original. This work (in part or in full) has not been submitted to any University for the award of a Degree or a Diploma. I have properly acknowledged the material collected from secondary sources wherever required. I solely own the responsibility for the originality of the entire content.

Date:

(Timmy Francis)

# CERTIFICATE

I feel great pleasure in certifying that the thesis entitled "Atmospheric Sulphur Dioxide and Sulphate Aerosols: Spatial and Seasonal Variability" by Timmy Francis under my guidance. He has completed the following requirements as per Ph.D. regulations of the University

(a) Course work as per the university rules

- (b) Residential requirements of the university
- (c) Presented his work in the departmental committee

(d) Published/accepted minimum of one research paper in a referred research journal.

I am satisfied with the analysis of data, interpretation of results and conclusions drawn.

I recommend the submission of thesis.

Date:

Name and designation of supervisor Professor M. M. Sarin, Senior Professor

Countersigned by Head of the Department

# Dedicated

To

My Father, Mother and my Wife

#### Acknowledgement

This thesis work has greatly benefited from the motivation, encouragement and support I am offered by many people.

First and foremost, I express my deepest gratitude to Prof. M. M. Sarin, my thesis supervisor, for providing me with the opportunity to work in the field of atmospheric chemistry and guiding me all through this endeavour. I greatly benefited from his expertise in the subject and his amazing experimental handle. The opportunities he provided me for trying out many innovative research ideas and techniques, some of them for the first time in the country, helped me reinforce my confidence to take up such initiatives in my future research career.

I am thankful to Prof. A. K. Singhvi, for providing me with the opportunity to work with him for some time during my research fellow tenure and learn many interesting experimental techniques including TL, OSL and ESR spectroscopy in his Luminescence Laboratory at PRL. I like to express my gratitude to Prof. R. Ramesh and Prof. S. Krishnaswami for their valuable comments and suggestions about my manuscripts.

I am deeply grateful to Prof. J. N. Goswami, Director, PRL and Prof. A. S. Joshipura, Dean, PRL, for extending all support and facilities to benefit my thesis work. I thank the academic committee members, PRL, for timely review of my work and for the valuable inputs. Special thanks to Prof. R. Ramesh, Prof. S. K, Bhattacharya, Dr. D Banerjee and Dr. S. K, Singh for their informative lectures during course work.

I am thankful to all members of the Chemistry Lab for their help and support during my thesis work. I thank Mr. A. K, Sudheer for his help while operating the Ion Chromatograph. I acknowledge Dr. R Rengarajan and Dr. Ravi Bhushan for their cooperation and suggestions during my thesis work. It's my pleasure to thank J. P. Bhavsar for his help and for providing a homely environment in the lab. I thank my collegues Ashwini, Kirpa, Srinivas, Prashant, Rahaman, Gyan, Vineet, Satinder, and Jayati, for their help and support. Discussion with my seniors, Dr. Morthekai and Dr. Neeraj helped me a lot in this thesis work. I duly acknowledge the help of Sneha, and Shantaben.

Thanks are also due to Prof. N. Bhandari, Prof. H. Chandra, Drs., J. S. Ray, P. Sharma, and Bhushit Vaishnav for their kind support and advices.

I like to thank all the staff-members of the Library, Computer Centre, Workshop, Administration, Dispensary and Maintenance section of PRL for their assistance and cooperation.

The support and help from the staff members of Mt. Abu Observatory and NESAC, Shillong during the sample collections is duly acknowledged. I am thankful to Dr. P. P. Nageshwara Rao, former director, NESAC for the support and logistics he extended towards the sampling at NESAC.

The memorable moments of PRL TV room, Volleyball and badminton matches are pleasant and unforgettable. Thanks to all my colleagues and friends in PRL, for a very pleasing environment.

I am grateful to the GEOS-Chem support team in the Harvard University Atmospheric Chemistry Modelling Group especially to Claire Carouge, Bob Yantosca and Philippe Le Sager, for their valuable guidance and support during the installation and test run of the GEOS-Chem Model.

Finally, but with most respect, I extend my deepest gratitude to my parents, Sri. Francis. C. A and Smt. Rosamma Francis for the constant efforts they put in for my academic growth. I am extremely thankful to my wife Anu Abraham for the unconditional support and encouragement she provided during the final stages of my thesis work.

#### **ABSTRACT:**

Sulphur gases, including sulphur dioxide (SO<sub>2</sub>), play multi-roles in the chemistry of global troposphere and in the biogeochemical sulphur cycle. Assessing the spatio-temporal variability in the S-ratio - the molar ratio of sulphate  $(SO_4^{2-})$  to total sulphur compounds  $(SO_x = SO_2 + SO_4^{2-})$ , which is a measure of the atmospheric oxidation efficiency of SO<sub>2</sub> - via simultaneous measurement of SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> is the major theme of this thesis work. Towards this, studies were performed from three sites in India, namely Shillong (25.67°N, 91.91°E, 1064 m ASL), Mt. Abu (24.6° N 72.7°E, 1680 m ASL) and Ahmedabad  $(23.0^{\circ} \text{ N}, 72.6^{\circ} \text{ E}, 49 \text{ m ASL})$ . The experimental results are then compared with a chemical transport model, GEOS-Chem (v8-03-01), generated results. The model in turn is further used to assess the contribution of various atmospheric parameters, such as the OH radical, relative humidity (RH) and planetary boundary layer (PBL) height to the molar S-ratio values. The ambient SO<sub>2</sub> concentrations at Shillong, measured during March 2009 and January 2010 showed significant differences in magnitude, which is explained – based on back trajectory analysis performed using HYSPLIT and the model runs performed using GEOS-Chem (v8-03-01) - as due to a transient long range transport from the highly industrialised Perm region in Russia, during a major cold air outbreak preceding one of the dust storm events reported in China. At Mt. Abu, the ambient SO<sub>2</sub> measurements showed pronounced seasonality in the long range transport of polluted air parcel to the sampling site from the SO<sub>2</sub> source region located around the co-ordinates  $30^{\circ}$  N and  $75^{\circ}$  E – the region projected as the one with the highest SO<sub>2</sub> concentration in the GEOS-Chem generated plots for the Indian region. The experimentally obtained molar S-ratios over Mt. Abu showed a seasonal dependence with relatively low ratios recorded during Feb-March 2010 and high ratios during Nov-Dec 2009. Intermediate ratios were obtained during Sept-Oct 2009. These are explained based on the PBL height, OH radical concentration and RH variabilities. At Shillong an unusually low molar S-ratio of 0.03 was observed during the high SO<sub>2</sub> transport event in March 2009 suggesting suppressed oxidation efficiency of the atmosphere. The GEOS-Chem generated molar Sratios also showed a seasonal dependence in tandem with the experimental observations.

(Keywords: Sulphur Chemistry, GEOS-Chem, Asian Pollutant Outflow, molar S-ratio)

### **CONTENTS**

Acknowledgements

List of Tab	les	xi
List of Figu	ires	xii - xvi
Chapter 1:	Introduction	(1-13)
1.1.	Introduction	1
1.2.	The Sulphur Chemistry in the Atmosphere: Homogeneou	is and $\Delta$
1.3.	S-ratio: The Atmospheric SO <sub>2</sub> oxidation efficiency	·
	indicator	6
1.4.	Chemical Transport Modeling Studies: Major Roles	7
1.4.1.	GEOS-Chem as a tool: Literature survey on important	
	works employing this Modeling tool	9
1.5.	Objectives of Present Study	12
1.6.	Thesis Outline	13
Chapter 2:	Materials and methods	(14-35)
2.1.	Introduction	14
2.2.	Site description	14
2.2.1	Mount Abu $(24.6^{\circ} \text{ N } 72.7^{\circ} \text{E}, 1680 \text{ m asl})$	14
2.2.1.	Ahmedabad $(23.0^{\circ} \text{ N}, 72.6^{\circ} \text{ E}, 49 \text{ m asl})$	15
2.2.2.	Shillong (25.67 <sup>0</sup> N, 91.9 <sup>0</sup> E, 1064 m asl)	16
2.3.	Experimental Setup	16
2.3.1	For SO <sub>2</sub> measurement	16
2.3.1.1.	The UV fluorescence SO <sub>2</sub> Monitor	16
2.3.1.2.	The dynamic gas calibrator (Thermo— 146i)	19
2.3.1.3.	Calibration of the SO <sub>2</sub> Analyser	20
2.3.2.	For $SO_4^{2-}$ measurements	22
2.4.	Trajectory Analysis	25
2.5.	GEOS- Chem Model Description	25
2.5.1.	General Description	25
2.5.2.	Emission inventories included in the model runs	26
2.5.3.	Chemistry Mechanism	31
2.5.4.	Deposition Mechanism	33
2.5.5.	The Model Simulation: Options set in the input.geos file	33
2.5.6.	Various input parameters to the Model	34
2.6.	GAMAP Visualization Toolkit	35
2.7.	The molar S-ratio calculation	35

# Chapter 3:Spatio-temporal trends in the ambient SO2 levels:<br/>High rain fall versus semi-arid region(36-113)

3.1.	Effect of Asian Dust Storms on the Ambient SO <sub>2</sub>	
	Concentration over North-East India: A Case Study	36
3.1.1.	Introduction	36
3.1.2.	Results and Discussions	37
3.1.2.1.	Major Features during March 2009	37
3.1.2.1.1.	Interpreting the High $SO_2$ Values	38
3.1.2.1.1.1	Source Identification Based on HYSPLIT Trajectories	38
3.1.2.1.1.2	Source Identification Using GEOS-Chem Model	39
3.1.2.1.1.2.1	The Perm City, Russia	41
3.1.2.1.1.3.	Anomalies Detected in Local Meteorology	41
3.1.2.1.1.4.	Dust Storm Detection Using GEOS-Chem	43
3.1.2.1.1.4.1	Cold Air Outbreaks and Dust Storms in Asia	46
3.1.2.1.2.	Transport from Russian Region: Implication to the Asian	
	Pollutant Outflow	48
3.1.2.2.	SO <sub>2</sub> Time-Series Data (March 2009): Model Versus	
	Observations:	60
3.1.2.3.	Major Features during January 2010	60
3.1.2.4.	SO <sub>2</sub> Time-Series Data (January 2010): Model Versus	
	Observations	60
3.1.3.	Conclusions	63
3.2.	Ambient SO <sub>2</sub> concentration over a high altitude site in	
	semi-arid Western India: Seasonal variability	64
3.2.1.	Introduction	64
3.2.2.	Results and Discussions	65
3.2.2.1.	SO <sub>2</sub> Plots for different Months	65
3.2.2.2.	SO <sub>2</sub> Measurements at Mt. Abu	68
3.2.2.1	Major Features: February 2009	68
3.2.2.2.2.	Major Features: September – October 2009	71
3.2.2.3.	Major Features: November 2009	74
3.2.2.3.1.	Detection of SO <sub>2</sub> plume from a major Oil fire incident	76
3.2.2.4.	Major Features: December 2009	78
3.2.2.5.	Major Features: February 2010	81
3.2.2.6.	Major Features: March 2010	84
3.2.2.3.	Explaining the Diurnal Variations in SO <sub>2</sub> Conc. using	
	GEOS-Chem Model	86
3.2.2.3.1.	Relative contribution of PBL height and OH radical	
	conc. on the $SO_2$ levels	94
3.2.2.4.	Effect of long range transport on ambient SO <sub>2</sub> levels over	
	Mt. Abu	97
3.2.3.	Summary and Conclusion	100
3.3.	Ambient SO <sub>2</sub> concentration over an urban site	
	(Ahmedabad) in Western India	102
3.3.1.	Introduction	102
3.3.2.	Major Features: April 2010	103

3.3.3.	Major Features: May 2010	105
3.3.4.	Major Features: July 2010	107
3.3.5.	Major Features: August 2010	109
3.3.6.	Major Features: September 2010	111
3.3.7	Summary and Conclusion	112

### **Chapter 4:** The $SO_2$ to $SO_4^{2-}$ conversion efficiency of the

	atmosphere under various environmental	conditions:
	-	(114 - 132)
4.1.	Introduction	114
4.2.	Results and Discussions	115
4.2.1.	The molar S-ratios at Mt. Abu	115
4.2.1.1.	The SO <sub>2</sub> and SO <sub>4</sub> <sup><math>2^{-}</math></sup> variability over Mt. Abu: Major	
	Observations	118
4.2.1.1.1.	September 2009	118
4.2.1.1.2.	October 2009	120
4.2.1.1.3.	November 2009	120
4.2.1.1.4.	December 2009	122
4.2.1.1.5.	February 2010	123
4.2.1.1.6.	March 2010	124
4.2.2.	The molar S-ratios at Shillong	125
4.2.2.1.	The SO <sub>2</sub> and SO <sub>4</sub> <sup><math>2^{-}</math></sup> variability over Shillong: Major	
	Observations	125
4.2.2.1.1.	March 2009	125
4.2.2.1.2.	January 2010	128
4.3.	Summary and Conclusions	130

### Chapter 5: Factors influencing the S-ratio: A GEOS-Chem model based study (133 - 163)

5.1	Introduction		133
5.2.	The seasonal variation in S-ratio from GEOS-Chem mode	el	133
5.3	Major parameters controlling the S-ratio: The model result	lts	135
5.3.1	OH radical concentration versus PBL height variations		135
5.3.2	OH radical concentration versus RH: The homogeneous		
	versus heterogeneous phase chemistry		145
5.3.3	Effect of Atmospheric Dust load on the S-ratio over Mt. A	Abu	151
5.3.4.	Effect of Transport on the S-ratio over Mt. Abu		152
5.3.5	Effect of Dry deposition on the molar S-ratio over Mt. Ab	ou	153
5.4	Diurnal variation in S-ratio		155
5.5	Variation in S-ratio as function of altitude above ground l	evel	159
5.5	Summary and Conclusion		162
Chapter 6:	Synthesis and Scope of Future Research (1	64-1	79)
6.1.	Synthesis		164
6.2.	Scope of future research		178
	References	(180-1	189)
	List of Publications		190

### List of Tables

Table	s Content	page
2.1	Specifications for the SO <sub>2</sub> Analyser (Thermo - Model 43i-TLE)	19
2.2	Details of Aerosol Samples collected from the high-altitude	
	remote site Mt. Abu for the sulphate measurements	24
2.3	Details of Aerosol Samples collected from the high-rainfall	
	site Shillong for the sulphate measurements	24
2.4	The various emission inventories used in the model runs	27
2.5	The various Tracers in the GEOS-Chem model for the standard run	32
2.6	The various options set under the "Convection Menu", "Aerosol	
	Menu", "Deposition Menu" and "Chemistry Menu" used	
	in the model runs	34
4.1	The mean and median of the molar S-ratio values obtained	
	experimentally over Mt. Abu during different sampling periods	117
4.2	The mean and median of the molar S-ratio values obtained	
	experimentally at Shillong during different sampling periods	125

### List of Figures

Figur	res Content	Page
2.1	SO <sub>2</sub> Analyser (Thermo-Model 43i TLE) flow Schematic	17
2.2	The calibration plot for the SO <sub>2</sub> analyser	21
2.3	Typical chromatogram obtained for separation of anions in	
	water soluble extract of aerosol samples	22
2.4	Repeat measurements of the chemical species $SO_4^{2-}$ (ppm) in	
	water extract of aerosol samples.	23
3.1.1	The measured $SO_2$ time series profile during March 2009 at	•
212	the sampling site, Shillong	38
3.1.2	The /-day back trajectories originating at the sampling site	40
212	Wind speed and wind direction during the compling period	40
3.1.3	obtained from nearby AWS	12
314	Relative humidity during the sampling period obtained from	42
5.1.7	nearby AWS	42
3.1.5	Atmospheric pressure during the sampling period, obtained	12
0.1210	from nearby AWS	43
3.1.6	The Mineral Dust Optical Depth (MOPD) profile obtained during	_
	10 <sup>th</sup> to 20 <sup>th</sup> of March 2009 from GEOS-Chem	45
3.1.7	The Trajectory Matrix plotted using HYSPLIT for the cold air	
	out break period	47
3.1.8	The 7- day back trajectories showing the air parcel from Russian	
	region reaching the Pacific during the dust storm events	48
3.1.9	SO <sub>2</sub> profile averaged for the first half of every month for 2009 from	l
	GEOS-Chem model runs showing the SO <sub>2</sub> peaking over the Perm	
2 1 10	region in Russia, during the months Nov, Dec, Jan, Feb and Mar	53
3.1.10	NOx, Peroxyacetyl Nitrate (PAN), Lumped Peroxypropionyl	
	Nitrate (PPN), HNO <sub>3</sub> , HNO <sub>4</sub> , $C_3H_8$ , $C_2H_6$ , SO <sub>4</sub> , NH <sub>4</sub> , Inorganic	
	surplui Milates (M11) and Lumped Alkyi Milate (K4N <sub>2</sub> ) promes	
	model runs	57
3.1.11	$N_2O_5$ NH <sub>2</sub> hydrophilic black carbon (BCPI) hydrophilic	51
	organic carbon (OCPI) hydrophobic black carbon (BCPO)	
	hydrophobic organic carbon (OCPO) profiles averaged for the	
	first half of March 2009 from GEOS-Chem model runs	59
3.1.12	SO <sub>2</sub> time series profile generated using GEOS-Chem for the	
	sampling period in March 2009 for the nearest co-ordinates	
	$(26^{\circ}N, 90^{\circ}E)$	61
3.1.13	The measured SO <sub>2</sub> time series profile during January 2010 at the	
	sampling site, Shillong	61
3.1.14	The 7-day back trajectories originating at the sampling site plotted	
• • • =	using HYSPLIT for January 2010	62
3.1.15	$SO_2$ time series profile generated using GEOS-Chem for the	
	sampling period in January 2010 for the nearest co-ordinates $(2c^0)$ N = $c^0$ N	
	$(20^{\circ} N, 90^{\circ} E)$	63

3.2.1	SO <sub>2</sub> concentration over the Indian region averaged for the first	
	half of each month of the year 2009 showing the major source	
	regions, generated using the GEOS-Chem model	67
3.2.2	The wind back trajectories plotted for various days during	
	the sampling period in Feb '09 generated using HYSPLIT	69
3.2.3	The time series $SO_2$ profile recorded during the sampling	
	period in February 2009. at Mt. Abu	70
3.2.4	The diurnal pattern for the $SO_2$ concentration measured during the	
01211	sampling period in February 2009 at Mt. Abu	70
325	The wind back trajectories plotted for various days during the	70
0.2.0	sampling period in Sept-Oct '09 generated using HVSPI IT	72
326	The SO <sub>2</sub> time series spectrum recorded during the sampling period in	12
5.2.0	Sant Oct '00 at Mt. Abu	73
377	The diurnal pattern for the SO, concentration measured during the	15
3.4.1	The diurnal patient for the $SO_2$ concentration measured during the sameling period in Sect. Oct 2000 at Mt. Abu	72
270	Sampling period in Sept-Oct 2009 at Mi. Adu	15
3.4.0	ampling period in New '00 generated using LIVSDLIT	74
220	The SO time period in Nov 09 generated using HTSPLIT	/4
3.2.9	The $SO_2$ time series spectrum recorded during the sampling period	75
2 2 10	in Nov 09 at Mt. Abu	15
3.2.10	The diurnal pattern for the $SO_2$ concentration measured during the	
2 2 1 1	sampling period in November 2009 at Mt. Abu	75
3.2.11	The wind back trajectories plotted for plume transport days in	
	Nov '09 generated using HYSPLIT	77
3.2.12	The $SO_2$ spikes detected at Mt. Abu when plumes from the Jaipur	
	Oil fire reached the sampling site	78
3.2.13	The wind back trajectories plotted for various days during the	
	sampling period in December '09 generated using HYSPLIT	79
3.2.14	The $SO_2$ time series spectrum recorded during the sampling	
	period in December '09 at Mt. Abu	80
3.2.15	The diurnal pattern for the SO <sub>2</sub> concentration measured during the	
	sampling period in December 2009 at Mt. Abu	80
3.2.16	The SO <sub>2</sub> time series spectrum recorded during the sampling period	
	in February 2010 at Mt. Abu	81
3.2.17	The wind back trajectories plotted for various days during the	
	sampling period in February 2010 generated using HYSPLIT	82
3.2.18	The diurnal pattern for the SO <sub>2</sub> concentration measured during the	
	sampling period in February 2010 at Mt. Abu	83
3.2.19	The SO <sub>2</sub> time series spectrum recorded during the sampling period	
	in March 2010 at Mt. Abu	84
3.2.20	The wind back trajectories plotted for various days during the	
	sampling period in March 2010 generated using HYSPLIT	85
3.2.21	The diurnal pattern for the SO <sub>2</sub> concentration measured during the	
	sampling period in March 2010 at Mt. Abu	86
3.2.22	The diurnality pattern observed in the GEOS-Chem generated	
	$SO_2$ time series data for different months of the year 2009	88
3.2.23	The diurnality pattern observed in the GEOS-Chem generated PBL	
-	height data for different months of the year 2009	90
3.2.24	The diurnality pattern observed in the GEOS-Chem generated OH	

	radical concentrations data for different months of the year 2009	92
3.2.25	OH radical concentration during different months of the year 2009	
	over $(26^{\circ} \text{ N}, 75^{\circ} \text{ E})$ generated using GEOS-Chem	93
3.2.26	PBL heights during different months of the year 2009 over	
	$(26^{\circ} \text{ N}, 75^{\circ} \text{ E})$ generated using GEOS-Chem	93
3.2.27	Three dimensional graphs showing the SO <sub>2</sub> concentration dependence	
	on the OH radical levels and PBL heights for different months of the	
	vear 2009 The time series SO <sub>2</sub> OH and PBL heights were obtained	
	from the GEOS-Chem model	96
3 7 78	Percent Difference in the SO <sub>2</sub> concentration in the absence of	70
5.2.20	Transport for different months of the year 2009 calculated	
	using GEOS Chem model runs	08
3 7 70	The time series percent decrease in the SO, levels in the absence	90
3.2.29	of the transport mechanism for different months of the year 2000	100
221	The SO time series spectrum recorded during the sempling period	100
3.3.1	The $SO_2$ time series spectrum recorded during the sampling period	102
222	In April 2010 at Anneoadad	105
3.3.2	The diurnal pattern for the $SO_2$ concentration measured during the	104
	sampling period in April 2010 at Anmedabad	104
3.3.3	The back trajectory matrix plotted for 15° of April 2010 for the	104
	sampling region	104
3.3.4	The $SO_2$ time series spectrum recorded during the sampling period	105
~ ~ -	in May 2010 at Ahmedabad	105
3.3.5	The diurnal pattern for the $SO_2$ concentration measured during the	100
	sampling period in May 2010 at Ahmedabad	106
3.3.6	The back trajectory matrix plotted for 15 <sup>th</sup> of May 2010 for the	
	sampling region	106
3.3.7	The $SO_2$ time series spectrum recorded during the sampling period	
	in July 2010 at Ahmedabad	107
3.3.8	The diurnal pattern for the $SO_2$ concentration measured during the	
	sampling period in July 2010 at Ahmedabad	108
3.3.9	The back trajectory matrix plotted for 15 <sup>th</sup> of July 2010 for the	
	sampling region	108
3.3.10	The SO <sub>2</sub> time series spectrum recorded during the sampling	
	period in August 2010 at Ahmedabad	109
3.3.11	The diurnal pattern for the SO <sub>2</sub> concentration measured during	
	the sampling period in August 2010 at Ahmedabad	110
3.3.12	The back trajectory matrix plotted for 15 <sup>th</sup> of August 2010 for the	
	sampling region	110
3.3.13	The SO <sub>2</sub> time series spectrum recorded during the sampling period	
	in September 2010 at Ahmedabad	111
3.3.14	The diurnal pattern for the SO <sub>2</sub> concentration measured during the	
	sampling period in September 2010 at Ahmedabad	111
3.3.15	The back trajectory matrix plotted for 15 <sup>th</sup> of September 2010	
	for the sampling region	112
4.1	Experimentally obtained molar S-ratios during different sampling	
	periods at Mt. Abu showing its temporal variability	116
4.2	The $SO_4^{2-}$ and median of the $SO_2$ concentrations recorded during	
	each sampling interval for the sampling period in September 2009	

	over Mt. Abu showing its systematic variation	119
4.3	The $SO_4^{2^2}$ and median of the $SO_2$ concentrations recorded during	
	each sampling interval for the sampling period in October 2009	
	over Mt. Abu showing its systematic variation	120
4.4	The $SO_4^{2-}$ and median of the $SO_2$ concentrations recorded during	
	each sampling interval for the sampling period in November 2009	
	over Mt. Abu showing its systematic variation	121
4.5	The $SO_4^{2-}$ and median of the $SO_2$ concentrations recorded	
	during each sampling interval for the sampling period in	
	December 2009 over Mt. Abu showing its systematic variation	122
4.6	The $SO_4^{2-}$ and median of the $SO_2$ concentrations recorded	
	during each sampling interval for the sampling period in	
	February 2010 over Mt. Abu showing its systematic variation	123
4.7	The $SO_4^{2-}$ and median of the $SO_2$ concentrations recorded	
	during each sampling interval for the sampling period in March 2010	
	over Mt. Abu showing its systematic variation	124
4.8	The $SO_4^{2-}$ and median of the $SO_2$ concentrations recorded during	
	each sampling interval for the sampling period in March 2009 at	
	Shillong showing its systematic variation	127
4.9	The molar S-ratio values calculated during different sampling interval	S
	for the sampling period in March 2009 at Shillong. The trend seen	
	from the regression line is a dip in the oxidation efficiency during	
	the initial days of the sampling followed by a steady increase	128
4.10	The $SO_4^{2-}$ and median of the $SO_2$ concentrations recorded during	
	each sampling interval for the sampling period in January 2010 at	
	Shillong showing its systematic variation	129
5.1	Seasonal variation in the molar S-ratio calculated from the	
	GEOS-Chem model runs	134
5.2	OH radical concentration recorded on the 1 <sup>st</sup> day of each month	
	of the year 2009, generated using GEOS-Chem for the Indian	region,
	showing its seasonal variability	137
5.3	PBL height recorded on the 1 <sup>st</sup> day of each month of the year	
	2009, generated using GEOS-Chem for the Indian region, showing	
	its seasonal variability	139
5.4	The variation in the molar S-ratio as function of OH radical	
	concentration and PBL height plotted for different months of the	
	year 2009 for the co-ordinates $(26^{\circ} \text{ N}, 75^{\circ} \text{ E})$	142
5.5	The relative humidity (RH) recorded on the 1 <sup>st</sup> day of each month	
	of the year 2009, generated using GEOS-Chem for the Indian	
	region, showing its seasonal variability	147
5.6	The variation in the molar S-ratio as functions of OH radical	
	concentration and RH plotted for different months of the year 2009	
	for the co-ordinates $(26^{\circ} \text{ N}, 75^{\circ} \text{ E})$	149
5.7	The Percentage difference in S-ratio values in the absence of	
	dust emission	152
5.8	The Percentage difference in S-ratio values in the absence of	
	Transport	153
5.9	The Percentage difference in S-ratio values in the absence	

	of dry deposition	155
5.10	The diurnal variation observed for the molar S-ratio for different	
	months of the year 2009, using GEOS-Chem	158
5.11	Variation in molar S-ratio as function of altitude above ground level	
	for the summer month, May 2009	160
5.12	Variation in molar S-ratio as function of altitude above ground level	
	for the month, July 2009	161
5.13	Variation in molar S-ratio as function of altitude above ground level	
	for the winter month, December 2009	161

## Chapter 1

### Introduction

#### **1.1 Introduction**

Systematic monitoring of sulphur gases in the troposphere can help assess their effects on the global climate in view of the multi-roles they play in the chemistry of global troposphere [e.g., [Andreae, 1990; Andreae and Jaeschke, 1992; Bates et al., 1987; Cullis and Hirschler, 1980; Freney et al., 1983; Rodhe and Isaksen, 1980; Saltzman and J., 1988; Toon et al., 1987]. Out of all the major sulphur gases including sulphur dioxide, dimethyl sulphide, hydrogen sulphide, carbon disulfide, and carbonyl sulphide, SO<sub>2</sub> has special significance for it is an important air pollutant. Sulfur dioxide plays important roles in the atmospheric sulphur cycle through its role in the formation of new aerosols and the modification of existing aerosols. It influences the oxidizing power of the atmosphere and air quality, cause acid rain [e.g., [Gerhardsson et al., 1994; SCHINDLER, 1988]], and modify atmospheric radiative forcing pattern via gasphase chemistry and particle formation.

Fossil fuel combustion is the major source of anthropogenic sulphur dioxide (SO<sub>2</sub>) in urban areas, aside from natural sources. At least 90% of the sulphur present in fossil fuels enters gas phase as sulphur dioxide (SO<sub>2</sub>) during combustion and is released to the atmosphere ([Benkovitz et al., 1996; Spiro et al., 1992]). An enhanced role of SO<sub>2</sub> in global climate change is now anticipated making it essential to precisely quantifying their levels. As per IPCC 2007, the estimates of global SO<sub>2</sub> emissions range from 66.8 to 92.4 TgS yr<sup>-1</sup> for anthropogenic emissions and from 91.7 to 125.5 TgS yr<sup>-1</sup> for total emissions in the 1990s. There has been a regional shift in the emissions of SO<sub>2</sub> from the US and Europe to south-east Asia with implications to the shift in the atmospheric radiative forcing patterns in these regions ([Boucher and Pham, 2002; IPCC, 2007; Pham et al., 2005; Smith et al., 2004]. [Guttikunda et al., 2003] projected

mega cities in Asia as one of the large emission sources of SO<sub>2</sub>. The Asian region is characterized by a rapid increase in the energy consumption for a fast growing population and emerging economy. This rapid growth in fossil fuel usage in Asia, especially the increase in the use of high sulfur coal for fuel, has raised fears about the potential impact of  $SO_2$  on the global climate. For example there were direct observations of SO<sub>2</sub> getting transported from sources in east Asia to the atmosphere over western Pacific during NASA (Pacific Exploratory Mission) PEM West A and B missions [Thornton et al., 1996; Thornton et al., 1997]. Similarly many instances of long-range transport of gases and aerosols to the Pacific were observed [Andreae et al., 1988; Bailey et al., 2000; Clarke et al., 2001; Duce et al., 1980; Harris et al., 1992; Hoell et al., 1997; Jaffe et al., 1999; Jaffe et al., 2003a; Jaffe et al., 2003b; Moore et al., 2003; Perry et al., 1999; Prospero et al., 2003; Shaw, 1980; Steding and Flegal, 2002] with the highest number of such instances reported during springtime [Duce et al., 1980; Jaffe et al., 2003a; Jaffe et al., 2003b; Moore et al., 2003; Prospero et al., 2003] when strong mid-latitude westerly winds are present [Andreae et al., 1988; Bey et al., 2001; Prospero et al., 2003; Wilkening et al., 2000; Xiao et al., 1997]. Similarly, [Merril et al., 1989] found a broad annual maximum in the Asian dust concentrations over the North Pacific during February to May - the months with the maximum number of dust storm events report in the Chinese region. [Jaffe et al., 1999], showed evidences for the surface emission from Asia entering the free troposphere and transporting to North America in as minimum as 6 days. The mechanisms responsible for the transport of SO<sub>2</sub> from its sources in northeast Asia across the Pacific and its impact on the Pacific troposphere have not been fully resolved. This thesis study has addressed some aspects of this long range transport of SO<sub>2</sub> to the Pacific, especially those from the Russian region and transporting across northeast India to the Pacific, during the Asian dust storm events in spring.

As per [IPCC, 2007], the abundance and radiative properties of atmospheric aerosols represent an internal forcing mechanism for climate change and one of the most uncertain factors of the Earth's climate system. Heavy aerosol loading can affect the energy balance [Li et al., 2007] and the evolution of the planetary boundary layer [Yu et al., 2002]. As per [Li, 2004], the anthropogenic

aerosol loading in the Chinese region has drastically increased over the last few decades, and may have a strong impact on regional climate. The Asian aerosols is found to have a high absorbance of solar radiation attributed to their internal mixing [e.g., [Chameides, 1999; Cheng et al., 2009; Höller et al., 2003]] and/or soot adhered to the surface of mineral dust particles [Chaudhry et al., 2007; Chaudhry, 2008]. Systematic studies have shown that the recent weakening of the East Asian summer monsoon [Xu et al., 2006], reduced cloudiness [Qian et al., 2006] and the "north drought south flood" climate anomaly [Xu, 2001] over China, are related to this high aerosol loading over this region. Out of the major suspended particulate matters, one of the prevalent components over this region is sulphate.

It is known that sulphate aerosols, the oxidation product of sulphur gases, influences global as well as regional climate via acidification of environment [Gerhardsson et al., 1994; SCHINDLER, 1988] and perturbation of atmospheric radiative forcing through new particle formation and cloud microphysics with implication to introduce large uncertainties in the assessments of climate change [*Solomon*, 2007]. These aerosols affect radiative forcing directly by reflecting the incoming solar radiation and indirectly by changing the albedo and lifetime of clouds [Breon et al., 2002; Gassó, 2008]. The global mean direct radiative forcing by sulphate aerosols is estimated to be  $-0.4\pm0.2$  Wm<sup>-2</sup> [Adams et al., 2001; Haywood and Boucher, 2000; Ramaswamy, 2001; Takemura et al., 2005, IPCC, 2007]. As per the IPCC, 2007, there is a high degree of uncertainty prevailing in the understanding of the oxidation process of sulphur species in the atmosphere. The SO<sub>2</sub> once converted to sulphuric aerosols can have long residence times (up to a few years), depending mostly on their altitudes in the atmosphere.

A comparative study aiming at understanding the differences in the ambient levels of  $SO_2$  and  $SO_4^{2-}$  over sites with different environmental characteristics can improve upon the current understanding about the oxidation process of  $SO_2$  in the atmosphere. Similarly observing the  $SO_2$  and  $SO_4^{2-}$  simultaneously over high rain fall regions can result in a better understanding of the heterogeneous phase oxidation of  $SO_2$  in the atmosphere. Data analysis

coupled with meteorology and atmospheric modelling can help understand the transport and chemistry occurring in the atmosphere and hence to reducing the uncertainty in the predications about climate change.

# **1.2.** The Sulphur Chemistry in the Atmosphere: Homogeneous and Heterogeneous Oxidation of SO<sub>2</sub>

Aerosol sulphate, as mentioned previously, is produced in the atmosphere predominantly by the oxidation of its precursor species  $SO_2$ . Atmospheric oxidation of  $SO_2$  occurs via both heterogeneous and homogeneous pathways and the oxidation rate increases with relative humidity [Sander and Seinfeld, 1976]. A large fraction of  $SO_2$  is converted by the heterogeneous reaction,

$$SO_2 + H_2O \rightarrow H_2SO_3$$

and the sulphite is oxidized either by reaction with ozone [Maahs, 1983]

$$SO_3^{2-} + O_3 \rightarrow SO_4^{2-} + O_2$$

or by H<sub>2</sub>O<sub>2</sub> [Seinfeld and Pandis, 1998]

 $HSO_3 + H_2O_2 \leftrightarrow SO_2OOH + H_2O$ 

#### $SO_2OOH^- + H^+ \rightarrow H_2SO_4$

or by reaction with catalytic metals. These reactions are responsible for the oxidation of SO<sub>2</sub> in cloud and fog droplets and on particles [Monn and Schaeppi, 1993; Seinfeld and Pandis, 1998] such as dust. The aqueous-phase conversion of dissolved SO<sub>2</sub> to sulphate is considered the most important chemical transformation in cloud water. The dissolution of SO<sub>2</sub> in water results in the formation of three chemical species: hydrated SO<sub>2</sub> (SO<sub>2</sub>.H<sub>2</sub>O), the bisulphate ion (HSO<sub>3</sub><sup>-</sup>), and the sulphite ion (SO<sub>3</sub><sup>2-</sup>). At the pH range of atmospheric interest (pH= 2-7), most of the sulphate is in the form of HSO<sub>3</sub><sup>-</sup>, whereas at low pH ( pH<2 ), all the sulphate occur as SO<sub>2</sub>. H<sub>2</sub>O. At higher pH values (pH > 7), SO<sub>3</sub><sup>2-</sup> is the preferred sulphate state. Oxidation of SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub> can happen via the following homogeneous phase reaction also [Seinfeld and Pandis, 1998]

 $SO_2 + . OH + M \rightarrow HOSO_2 . + M$  $HOSO_2 . + O_2 \rightarrow HO_2 . + SO_3$  $SO_3 + M + H_2O \rightarrow H_2SO_4 + M$ 

where M is any third molecule capable of taking up the excess kinetic energy. The sulphuric acid thus produced then condenses onto aerosols and a fraction of it nucleates with water vapour ( $H_2O$ ) and ammonia ( $NH_3$ ) in the vapour phase to produce sulphate aerosols [Kulmala et al., 2004]. The lifetime of SO<sub>2</sub> based on reaction with the OH radical, at typical atmospheric levels of OH, is about a week.

The hydroxyl radical required for the above reaction is produced via the following photochemical reactions

 $H_2O_2 + hv \rightarrow OH + OH$   $O_3 + hv \rightarrow O_2 + O (^1D)$  $O (^1D) + H_2O \rightarrow 2OH$ 

where ozone can be produced vi the photolysis of NO<sub>2</sub> [Seinfeld and Pandis, 1998]

 $NO_2 + hv \rightarrow NO + O$  $O + O_2 + M \rightarrow O_3 + M$ 

The above reaction is the major path way of ozone production in the atmosphere. The ozone thus produced reacts with NO to regenerate  $NO_2$ 

$$O_3 + NO \rightarrow NO_2 + O_2$$

Ultimately the atmospheric OH radical is consumed via the following reaction of NO<sub>2</sub> with OH

$$OH + NO_2 + M \rightarrow HNO_3 + M$$

The hydroxyl radical is also removed efficiently from the atmosphere via the following reaction of OH radical with CO

$$CO + OH \rightarrow CO_2 + H$$

where the hydrogen atom thus formed reacts with  $O_2$  to form the hydroperoxyl radical

#### $H + O_2 + M \rightarrow HO_2 + M$

In areas characterized by high abundances of mineral dust, chemical uptake of  $H_2SO_4$  on to particles via the following reaction [Andreae and Crutzen, 1997; Dentener et al., 1996; Krueger et al., 2003] can occur.

#### $CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$

The physical loss mechanisms for the removal of atmospheric  $SO_2$  are via dry and wet depositions.  $SO_2$  is one of the gases that is reasonably efficiently removed from the atmosphere by dry deposition. At a dry deposition velocity of about 1 cm s<sup>-1</sup>, the lifetime of  $SO_2$  by dry deposition in a 1 km deep boundary layer is about 1 day. When clouds are present, the removal of  $SO_2$  can be enhanced even beyond that attributable to dry deposition.

#### 1.3. S-ratio: The Atmospheric SO<sub>2</sub> oxidation efficiency indicator

A factor, S-ratio, defined the ratio of particulate S (as  $SO_4^{2^-}$ ) to total S (as  $SO_2$  and  $SO_4^{2^-}$ ) can be used as a parameter to track the average formation efficiency of  $SO_4^{2^-}$  (i.e., the amount of  $SO_4^{2^-}$  produced per  $SO_2$  emitted from the emission sources) in the atmosphere for different seasons and environmental conditions. The ratio is an indicator of air mass age, chemical conversion efficiency and "en route" deposition.

Earlier studies [Hidy et al., 1978; Husar and Patterson, 1980] of the spatiotemporal variability of SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> point to the fact that the molar ratio of sulphate to total sulphur compounds (SO<sub>x</sub> = SO<sub>2</sub> + SO<sub>4</sub><sup>2-</sup>), termed S-ratio, show a seasonal dependence. [Kaneyasu et al., 1995], showed that the S-ratio can be used as measure of the formation efficiency of SO<sub>4</sub><sup>2-</sup>. Spatio-temporal changes in various atmospheric parameters directly influencing the chemical conversion efficiency of  $SO_2$  to  $SO_4^{2-}$  as well as differences in the loss rate of  $SO_2$  and  $SO_4^{2-}$  from the atmosphere by dry deposition, can cause the S-ratio vary spatially and seasonally.

Many atmospheric parameters can influence the atmospheric oxidation efficiency of  $SO_2$  and hence the S-ratio, such as OH radical concentration, atmospheric dust content, Planetary Boundary Layer Height variation, atmospheric water content, season dependent variation in the long range transport of pollutants to the sampling site, the variation in the dry deposition rate and so on. For example if the dust content in the atmosphere is very high, the heterogeneous oxidation of  $SO_2$  on dust surface may enhance the conversion of  $SO_2$  to  $SO_4^{2^2}$  and hence the S-ratio.

[Miyakawa et al., 2007], had suggested that seasonal variations in the conversion efficiency of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> could be due to seasonal variations in the boundary layer height and photochemical activity. They proposed that the higher boundary layer height for summer results in reduced loss rate of SO<sub>2</sub> by dry deposition which in turn cause an efficient oxidation of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> before loss onto the surface, with implication to an enhanced S-ratio. Similarly the production rate of OH radical, the major species responsible for SO<sub>2</sub> oxidation have a dependence on the incoming solar radiation intensity and the water vapour content in the atmosphere, giving way for a season dependent variation in the S-ratio. Similarly, the level of pollutants such as NO<sub>2</sub> and CO at the sampling site also could be important parameters affecting the OH radical levels and thus the oxidation efficiency of SO<sub>2</sub> in the atmosphere.

#### 1.4. Chemical Transport Modeling Studies: Major Roles

The experimental measurements of the various atmospheric pollutants in an ambient atmosphere provide only a snapshot of atmospheric conditions for that particular time and particular site. Interpreting such experimental observations many a time requires the support from a model of atmospheric processes which help in the formulation of effective strategies for solving air quality problems. Integrating the present understandings on individual atmospheric processes (chemistry, transport, removal etc.) to a mathematical model provide the necessary framework for integration of our understanding of individual atmospheric processes and study of their interactions, which is the basis of an atmospheric Chemical Transport Model. A combination of state-of-the-science measurements with state-of-the-science models is the best approach for making real progress toward understanding the atmosphere. [Seinfeld and Pandis, 1998]. Some of the important issues which can be dealt with a Chemical Transport Model are understanding the long range effects of various pollutants to locations lying far away - even on the other side of the globe, understanding the implications on an enhancement in the concentration of certain pollutants on the global climate as well as predicting the future climatic scenarios expected if the current emission patterns are continued helping policy makers to look for appropriate measures to tackle such issues.

A well established chemical transport model such as the GEOS-Chem global 3-D model of tropospheric chemistry (v8-03-01; http://acmg.seas.harvard.edu/geos/) driven by GEOS-5 assimilated meteorological observations - including winds, convective mass fluxes, mixed layer depths, temperature, clouds, precipitation, and surface properties - from the NASA Global Modelling and Assimilation Office (GMAO) model with provisions to incoporate emission patterns, meteorology, chemical transformations, and removal processes is a powerful tool to meet the above mentioned needs.

Since a clubbing of experimental observations with chemical transport modeling can better explain the state of the atmosphere, we have incorporated both experimental observations as well the GEOS-Chem Chemical Transport Model (v8-03-01; <u>http://acmg.seas.harvard.edu/geos/</u>) generated results in this thesis work. The experimental observations are many a time explained and interpreted with the model generated results and when a good correlation of the experimental results with those from the model are seen, the model in turn is further used to understand various parameters which directly or indirectly contribute to the experimental observations which was not possible with our available experimental set up.

# **1.4.1.** GEOS-Chem as a tool: Literature survey on important works employing this Modeling tool.

The GEOS-Chem 3-D global model (v8-03-01; http://acmg.seas.harvard.edu/geos/) used for comparison and interpretation of our experimental observations is a well known Chemical Transport Model developed by the Harvard University Atmospheric Chemistry Modeling Group and has many recent literatures to its credit. One of the most relevant works done using this model which has direct correlation with this thesis study is [Lee et al., 2009]. They developed an improved retrieval of sulphur dioxide (SO<sub>2</sub>) vertical columns from two satellite instruments (SCIAMACHY and OMI) that measure ultraviolet solar backscatter. For each SCIAMACHY and OMI observation, a local air mass factor (AMF) algorithm converts line-of-sight "slant" columns to vertical columns using altitude-dependent scattering weights computed with a radiative transfer model (LIDORT), weighted by relative vertical SO<sub>2</sub> profile (shape factor). They used the global atmospheric chemistry model (GEOS-Chem) to determine locally this shape factor. Absorption of radiation by mineral dust can reduce seasonal mean instrument sensitivity by 50%. Mean SO<sub>2</sub> shape factors simulated with GEOS-Chem and used in the AMF calculation were found to be highly consistent with airborne in situ measurements (INTEX-A and INTEX-B); differences would have affected the retrieved SO<sub>2</sub> columns by 10%. They showed that the seasonal mean SO<sub>2</sub> columns retrieved from SCIAMACHY and OMI for 2006 significantly spatially correlate with those from GEOS-Chem, in particular over the United States (r = 0.85 for SCIAMACHY and 0.82 for OMI). They also carried out a sensitivity study which confirmed the sensitivity of SCIAMACHY and OMI to anthropogenic SO<sub>2</sub> emissions.

[*Wang et al.*, 2008] in their work entitled "Global distribution of solid and aqueous sulfate aerosols: Effect of the hysteresis of particle phase transitions" simulated the partitioning between solid and aqueous phases of tropospheric sulfate-ammonium particles with the global 3-D chemical transport model (CTM),

GEOS-Chem. The simulation explicitly accounted for the hysteresis of particle phase transitions by transporting aqueous sulfate and three solid sulfate forms (namely, ammonium sulfate, letovicite, and ammonium bisulfate). They found that the solids mass fraction on a sulfate basis is 0.34, partitioned as 93% ammonium sulfate, 6% letovicite, and 1% ammonium bisulfate. They attributed the dominance of solids in the upper troposphere in part to high sulphate neutralization. The high sulfate neutralization was consistent with the few available observations in the upper troposphere.

[*Suntharalingam et al.*, 2008] in their work entitled "Global 3-D model analysis of the seasonal cycle of atmospheric carbonyl sulfide: Implications for terrestrial vegetation uptake" used the global 3-D simulation of atmospheric carbonyl sulfide (COS) using GEOS-Chem to interpret observations at a network of surface sites. The work tried to identify the primary factors underlying observed seasonal variations and to constrain COS uptake by terrestrial vegetation. They found that the dominant influences on seasonal variation of COS are terrestrial vegetation uptake in the northern extratropics, and ocean fluxes in the southern extratropics.

[*Zhang et al.*, 2010] in an attempt to understand the impact of the southeast Asian summer monsoon strength on the outflow of aerosols from South Asia, found GEOS-Chem very relevant for their study. They chose a relatively weak Southeast Asian summer monsoon (SEASM) year (1998) and a relatively strong year (2002) to examine the impact of the monsoon strength on the transport of organic carbon (OC) aerosol emitted from the South Asia using GEOS-Chem driven by the assimilated meteorological fields. They found that the simulated surface layer concentrations and column burdens of OC were much higher in the weak SEASM year 1998 than in the strong SEASM year 2002. Their sensitivity experiments with global OC emissions turned off except those over the South Asia showed that OC aerosol emitted from South Asia contributes to 50–70% of OC mass over southern China and 20–50% of OC over the western North Pacific between 850 hPa and 400 hPa in 1998.

[*Leung et al.*, 2007] used the GEOS-Chem model to study the impacts of enhanced biomass burning in the boreal forests in 1998 on tropospheric chemistry and the sensitivity of model results to the injection height of emissions. The Carbon monoxide levels had reached a record high in the northern extratropics in the late summer and fall of 1998 as a result of anomalously large boreal fires in eastern Russia and North America. They investigated the effects of these fires on CO and tropospheric oxidants using the global chemical transport model (GEOS-Chem). They found that it is essential to use both surface and column observations of CO to constrain the magnitude of the fire emissions and their injection altitude.

[*Hudman et al.*, 2007] in their study entitled "Surface and lightning sources of nitrogen oxides over the United States: Magnitudes, chemical evolution, and outflow" used observations from two aircraft during the ICARTT campaign over the eastern United States and North Atlantic during summer 2004, and interpreted with the global 3-D model of tropospheric chemistry (GEOS-Chem) to test current understanding of regional sources, chemical evolution, and export of NOx.

[*Fu et al.*, 2007] in their study entitled "Space-based formaldehyde measurements as constraints on volatile organic compound emissions in east and south Asia and implications for ozone" used a continuous 6-year record (1996–2001) of GOME satellite measurements of formaldehyde (HCHO) columns over east and south Asia to improve regional emission estimates of reactive nonmethane volatile organic compounds (NMVOCs), including isoprene, alkenes, HCHO, and xylenes. They compared the mean monthly HCHO observations to simulated HCHO columns from the GEOS-Chem chemical transport model using state-of-science, "bottom-up" emission inventories from Streets et al. (2003a) for anthropogenic and biomass burning emissions and Guenther et al. (2006) for biogenic emissions (MEGAN).

In an attempt to study the impact of transpacific transport of mineral dust in the United States [*Duncan Fairlie et al.*, 2007], used GEOS-Chem with the implementation of two dust mobilization schemes in the model (GOCART and DEAD) and found that the best simulation of North American surface observations with GEOS-Chem could be achieved by combining the topographic source used in GOCART with the entrainment scheme used in DEAD which they said reproduced the timing and distribution of Asian dust outbreaks in North America during April–May.

Some of the other recent works which showed the potential of this global Chemical Transport Model GEOS-Chem are, [*Yu et al.*, 2007], [*Xiao et al.*, 2008], [*Wang et al.*, 2007], [*Wu et al.*, 2009], [*Wang et al.*, 2008], [*Shim et al.*, 2008], [*Martin*, 2008], [*Millet et al.*, 2008], [*Selin and Jacob*, 2008], [*Fu et al.*, 2008], [*Martin*, 2008], [*Zhang et al.*, 2009], [*Xiao et al.*, 2008], [*Spracklen et al.*, 2009], [*Wu et al.*, 2008], and [*Rastigejev et al.*]

In view of the huge potential of this versatile global 3 Dimensional Chemical Transport Model GEOS-Chem in the study of the chemistry of atmosphere, we have incorporated GEOS-Chem model (v8-03-01; <u>http://acmg.seas.harvard.edu/geos/</u>) based studies also in this thesis work along with the experiments, to better interpret some of our experimental observations.

#### 1.5. Objectives of Present Study:

The specific objectives of the present study are

(a) To provide quantitative information on the surface level concentrations of gaseous SO<sub>2</sub> from two semi-arid sites located in western India and one high rainfall site located in North-East India. The sites have distinctly different emission sources, wind regimes, atmospheric transport and abundance of mineral dust.

b) To assess the temporal and spatial variability in the sulphur conversion ratio (molar S-ratio) - the molar ratio of  $SO_4^{2-}$  to total sulphur compounds  $(SO_x = SO_2 + SO_4^{2-})$ , which is a measure of the atmospheric oxidation efficiency of  $SO_2$  to  $SO_4^{2-}$ 

c) Calculate the molar S-ratios using a Chemical Transport Model, GEOS-Chem and compare with the experimentally observed molar S-ratios.

d) To study the relative contribution of various parameters controlling the Sratio such as dry deposition rate, atmospheric dust content, planetary boundary layer height, relative humidity, OH radical concentration, long range transport etc using GEOS-Chem Model.

- **1.6. Thesis Outline:** 
  - Chapter 1: Provides review of the work done in this field; rationale and objectives of the study.
  - Chapter 2: Describes the characteristic features of the sampling sites, the sampling and analytical protocol adopted for the sampling and chemical analyses of the collected aerosols. The chapter will also include discussion of the chemical transport model GEOS-Chem, and the various inputs to this model for this work.
  - Chapter 3: Discusses the spatio-temporal trends in the ambient SO<sub>2</sub> levels measured over the three different sampling locations, viz. Shillong, Mt. Abu and Ahmedabad. A comparison of the experimental time series data with the GEOS-Chem model generated results is also made in this chapter.
  - > Chapter 4: Discussion of the Spatio- temporal variability in the experimentally obtained molar S-ratio values from simultaneously measured  $SO_2$  and  $SO_4^{2-}$  is the core of this chapter. The reasons for the observed variabilities are discussed in this Chapter.
  - Chapter 5: "A GEOS-Chem Model based study on the relative contribution of different parameters in controlling the molar S-ratio" is the core discussion material for this chapter. The explanation for the spatiotemporal variability in the S-ratios comes mostly from this chapter and has implication to the current understanding on the sulphate - a major CCN with cooling effect in the atmosphere - formation over different environmental regimes.
  - Chapter 6: This chapter summarizes the important findings of the study and their implications to assessing the sulphate formation efficiency in the atmosphere, its spatio- temporal variability and the associated impact on climate change.

## Chapter 2

### **Materials and Methods**

#### 2.1. Introduction:

Accomplishing the specific objectives mentioned in Chapter 1, demanded very careful selection of sampling sites and devising very ingenious sampling protocols and experimental techniques. During the site selection process, efforts were taken to incorporate both urban as well as remote sites with distinctly different emission sources, wind regimes, atmospheric transport and abundance of mineral dust, which we thought, would help resolve the cross talk between various atmospheric kparameters controlling the SO<sub>2</sub> oxidation efficiency in the atmosphere. Accordingly three sites were selected, viz Mt. Abu ( $24.6^{0}$  N 72.7<sup>0</sup>E, 1680 m asl) – a remote high altitude site characterized by long range transport of pollutants and negligibly small number of local sources, Ahmedabad ( $23.0^{0}$  N, 72.6<sup>0</sup> E, 49 m asl) - characterized by a high abundances of mineral dust in the atmosphere [Rastogi and Sarin, 2006] and large number of strong local sources such as power plants and industrial establishments and high vehicular traffic, and a high rainfall site in North-East India, Shillong ( $25.67^{0}$  N,  $91.9^{0}$  E, 1064 m asl)

#### 2.2. Site description

#### 2.2.1. Mount Abu (24.6<sup>°</sup> N 72.7<sup>°</sup>E, 1680 m asl)

A high altitude remote site, Gurushikhar, Mt. Abu (24.6<sup>o</sup> N 72.7<sup>o</sup>E, 1680 m asl) with a more or less clean and stable atmosphere and having minimum contribution from local pollution sources was the first sampling site selected. Gurushikhar is the highest mountain peak in the southern end of Aravali range of mountains in western India. The annual rainfall at Mt Abu averages around 600-700 mm and occurs only during SW-monsoon. Gurushikhar exhibits free tropospheric characteristics during winter months, while during summer months

Gurushikhar gets accommodated within the boundary layer. The Gurushikhar site served as an ideal setting for sampling a relatively low dust environment compared to the second sampling site of Ahmedabad.

Earlier studies have shown that the atmospheric boundary layer height plays important roles in the columnar aerosol and gas concentrations as it strongly affects the vertical mixing of aerosols and gases [Krishnan and Kunhikrishnan, 2004]. During winter and post monsoon, atmospheric boundary layer height remains low due to less insolation at the Earth's surface and results in an inversion layer to oppose vertical mixing. In contrast, during Pre-monsoon and monsoon the height of boundary layer increases due to increased insolation (e.g. [Bhattacharya et al., 1996]. The special characteristics of occasional accommodation within the free troposphere as function of season makes the Gurushikhar site a very important one for the study reported here.

In addition, during favourable wind conditions, periodic long range transport of pollutants to Gurushikhar occurs, offering the opportunity to study the relative contribution of long range transport in controlling the ambient  $SO_2$  levels over this relatively pristine site.

#### **2.2.2.** Ahmedabad (23.0<sup>o</sup> N, 72.6<sup>o</sup> E, 49 m asl)

Ahmedabad (23.0<sup>°</sup> N, 72.6<sup>°</sup> E, 49 m asl) - a semiarid, industrialized urban location with several small and large-scale industries [Ramachandran and Kedia] - located in western India, ~ 500 km southeast of the Thar Desert and 100km north east of the Arabian sea, was the second sampling site selected. The city has an annual average rain fall of ~700 mm and the precipitation events seldom occur outside the SW monsoon period (Jun-Sep). Southwesterly winds are observed during May-Aug and the northeasterly winds in Nov-Feb. The typical wind fields over the study site are reported elsewhere [e.g., [*Rastogi and Sarin*, 2005]]. In the vicinity of about 10 km of the sampling location are residential and institutional complexes. The vehicular traffic peaks during the morning and evening hours. The pollutant transport from two coal-based thermal power plants, situated in the northeast at a distance of about 10 km (Sabamati:~350 MW per day) and 25 km

(Gandhi Nagar: 700 MW per day) are important sources of  $SO_2$  and airborne particles.

#### **2.2.3.** Shillong (25.67<sup>o</sup>N, 91.9<sup>o</sup>E, 1064 m asl)

The sampling site  $(25.67^{\circ} \text{ N}, 91.9^{\circ} \text{ E}, 1064 \text{ m asl})$  is located about 18 km away from the Shillong city, located on the Shillong Plateau at an elevation of 4,990 feet. The Shillong Plateau is an outlier of the plateau of peninsular India and is composed primarily of ancient rocks. The highest point is Shillong Peak, at 6,433 feet located 5 km south of the city of Shillong. It is on the Shillong Plateau, the only major pop-up structure in the northern Indian shield. Due to its latitude and high elevation Shillong has a sub-tropical climate with mild summers and chilly to cold winters. The region is subject to vagaries of the monsoon. The average annual rain fall is about 2200mm. The monsoon arrives in June and it rains almost until the end of August. Perched at an altitude of 4,990 feet above sea level, the Shillong city stretches for about 6 km on an elevated tract. It is situated on a plateau bound on the north by the Umiam gorge, on the northwest by the great mass of the Diengiei Hills that rise up to a height of 6077 feet above sea level, and on the northeast by the hills of the Assam valley. The proximity of this site to some of the highly polluted regions in North-East Asia and hence the possibility of long range transport makes this study location strategically important.

#### 2.3. Experimental Setup

#### 2.3.1 For SO<sub>2</sub> measurement:

The experimental set up comprised of a primary UV fluorescence  $SO_2$ Monitor (Thermo—43i Trace Level Enhanced (TLE)), an air compressor for producing zero- level (zero) gas and a dynamic gas calibrator (Thermo— 146i) for preparing diluted  $SO_2$  standard gas. Discussions on the performances of similar systems can be seen elsewhere [Igarashi et al., 2004; Luke, 1997; Luria et al., 1992]

#### 2.3.1.1. The UV fluorescence SO<sub>2</sub> Monitor:

The UV fluorescence  $SO_2$  Monitor (Thermo—43i Trace Level Enhanced (TLE)) operates on the principle that  $SO_2$  molecules absorb ultraviolet (UV) light and become excited at one particular wave length, followed by a decay to a lower energy state emitting UV light at a different wavelength. Specifically,

$$SO_2 + hv_1 \rightarrow SO_2^* \rightarrow SO_2 + hv_2$$

In the operation, the sample is drawn into the Model 43i TLE through the SAMPLE bulkhead, as shown in the Schematic of the Model 43i TLE  $SO_2$  UV fluorescence analyser in figure 2.1. The sample flows through a hydrocarbon "kicker", which removes hydrocarbons from the sample by forcing the hydrocarbon molecules to permeate through the tube wall. It operates on a selective permeation principle using differential pressure to force hydrocarbon molecules to pass through the tube wall. The differential pressure is created across the tube wall as sample gas passes through a capillary tube which reduces its pressure. The sample gas is then fed to the shell side of the hydrocarbon kicker. The SO<sub>2</sub> molecules pass through the hydrocarbon "kicker" unaffected.



Figure 2.1: SO<sub>2</sub> Analyser (Thermo-Model 43i TLE) flow Schematic

The sample then flows into the fluorescence chamber, where pulsating UV light excites the  $SO_2$  molecules. The condensing lens focuses the pulsating UV light into the mirror assembly. The mirror assembly contains four selective

mirrors that reflect only the wavelengths which excite  $SO_2$  molecules. As the excited  $SO_2$  molecules decay to lower energy states, they emit UV light which in turn is proportional to the  $SO_2$  concentration. The band pass filter allows only the wavelengths emitted by the excited  $SO_2$  molecules to reach the photomultiplier tube (PMT) which detects the UV light emission from the decaying  $SO_2$  molecules. The photo detector, located at the back of the fluorescence chamber, continuously monitors the pulsating UV light source and is connected to a circuit that compensates for fluctuations in the UV light.

As the sample leaves the optical chamber, it passes through a flow sensor, a capillary, and the "shell" side of the hydrocarbon kicker. The sample then flows to the pump and is exhausted out the EXHAUST bulkhead of the analyzer. The Model 43i TLE outputs the  $SO_2$  concentration to the front panel display and analog outputs, and also makes the data available over the serial or Ethernet connection.

Measurement Ranges	Preset Ranges : 0-10, 20, 50, 100, 200, 500 and 1000ppb
	0-20, 50, 100, 200, 500, 1000 and 2000 µg/m <sup>3</sup>
	Custom Ranges : 0-10 to 1000ppb 0-20 to 2000 $\mu$ g/m <sup>3</sup>
Flow rate	0.5 L/min.
Min. Detection Limit	0.05ppb (300 second averaging time)
Linearity	$\pm 1\%$ of full scale
Precision	1% of reading or 0.2ppb (whichever is greater)
Interferences	(EPA levels): < lower detectable limit except for the following:
	NO: Reads < 3ppb when tested at 500ppb
	M-Xylene: Reads < 1ppb when tested at 200ppb
	$H_2O$ : Reads < 2% of reading when tested at 2% $H_2O$ absolute
Zero Noise	0.025ppb RMS (300 second averaging time)
Drift	Zero Drift: <0.2ppb per day

	Span Drift: ±1% of full scale
Response Time	80 seconds (10 second average time)
Input Output	Outputs: Selectable Voltage, RS232/RS485, TCP/IP, 10 Status Relays, and Power Fail Indication (standard). 0-20 or 4-20mA Isolated Current Output (optional) Inputs: 16 Digital Inputs (standard), 8 0-10V Analog Inputs (optional)
Mounting	Bench, EIA, retrofit
Temperature Range [Operating]	Celsius: 5° to 40°C (20° to 30°C with EPA Designation) Fahrenheit: 41° to104°F(68° to 86°F with EPA Designation)

Table 2.1: Specifications for the SO<sub>2</sub> Analyser (Thermo - Model 43i-TLE)

Using pulsed fluorescence technology, the Model 43i-TLE measures the amount of sulphur dioxide in the air with an instrumental detection limit of 50 pptv (300 second averaging time). The lowest concentrations recorded in our measurements are > 1ppbv which is much above the minimum instrumental detection limit. The major specifications for Model 43i-TLE is given in table 2.1.

#### 2.3.1.2. The dynamic gas calibrator (Thermo—146i):

The model 146i Multi-gas calibrator dilutes calibration gases to precise concentrations. The diluted gases are used to perform zero, precision and Level 1 span checks, audits, and multipoint calibration of the 43i – TLE analyzer. The standard Model 146i hardware/plumbing configuration comprises gas and zero air flow controllers. The basic unit can handle three gas standards, controlled by individual solenoids. The zero air flow and the gas flow are regulated by mass flow controllers. The zero air controller is high flow (typically 10 slm full scale). The gas flow controller is low flow (typically 100 sccm). A Teflon mixing chamber is used to achieve complete mixing of the two components at the desired concentration level. This hardware/plumbing configuration allows precision gas dilution.

*Photometer:* The photometer in model 146i operates on the principle that sample gas molecules absorb UV light at a particular wavelength. The degree to which the UV light is absorbed is directly related to the SO<sub>2</sub> concentration as described by the Beer-Lambert Law:

$$\mathbf{I} = \mathbf{I}_0 \, \mathbf{e}^{-\mathbf{KLC}}$$

Where;

K = molecular absorption coefficient

L = Length of cell

 $C = SO_2$  concentration in parts per million (ppmv)

I = UV light intensity of sample with sample gas

#### 2.3.1.3. Calibration of the SO<sub>2</sub> Analyser:

While calibrating the SO<sub>2</sub> analyser, the following requirements had to be met: a) A calibration gas system capable of providing accurate levels of SO<sub>2</sub> calibration gas between zero and 80% of the full-scale range is required b) The calibration system must provide a flow rate of at least 0.5LPM for an instrument with the standard flow c) All calibration gas should be derived from local or working standards (such as cylinders or compressed gas or permeation devices) that are certified as traceable to an NIST primary standard d) Regulations typically require zero/span calibration when the instrument is newly installed, moved, repaired, interrupted for more than a few days, or when span or zero shift by more than 15% e) Record instrument reading for each concentration after allowing time for both gas generation system and instrument to stabilize and plot a graph of instrument readings against the SO<sub>2</sub> concentrations generated. This is the instrument calibration curve. All future measurements should be interpreted using this curve.

*Zero gas generation:* An SO<sub>2</sub> free (<0.0005ppm) air supply is required for the proper calibration and checkout of the instrument. We have used a commercial heatless air dryer filled with a mixed bed of activated charcoal and a 13X
Chapter - 2

molecular sieve for removing  $SO_2$  from compressed air which generated the required zero air with  $SO_2$  concentration below 0.0005 ppmv.

The UV fluorescence  $SO_2$  monitor was calibrated onsite every 10 days with standard  $SO_2$  gas (2ppmv with N<sub>2</sub> balance gas, Spectra, USA) and zero air. Shown in figure 2.2 is a typical calibration plot obtained for the  $SO_2$  analyser.



Figure 2.2: The calibration plot for the  $SO_2$  analyser for different span concentrations made from the standard  $SO_2$  gas (2ppmv with  $N_2$  balance gas, Spectra, USA).

*Zero/span Check:* The zero/span check procedure is normally performed any time a quick check of accuracy of the instrument is required. Normally, zero and span are checked daily. The span gas concentration used in the span check was kept between 70% and 90% of the full-scale range as per the instructions in the user's manual.

The integration time for the  $SO_2$  analyser was set at five minutes throughout the sampling and the  $SO_2$  raw data was periodically downloaded and fed to a computer through an ethernet port.

### **2.3.2.** For $SO_4^{2-}$ measurements

A high volume air sampler (Thermo) with a flow rate of  $1.12 \text{ m}^3/\text{min}$  and a cut off diameter of 2.5 micron (PM<sub>2.5</sub>) was used for collecting fine mode aerosol samples on Whatman cellulose filters ( $200x250\text{mm}^2$ ) from which sulphate was later extracted and measured. On average, an aerosol sample was collected every fourth hour during day time and every twelfth hour during night time (with some exception day-time samples collected for longer duration to improve signal to noise ratio).



Figure 2.3: Typical chromatogram obtained for separation of anions in water soluble extract of aerosol samples.

In the analytical procedure adopted for the measurement of sulphate  $(SO_4^{2-})$  in the aerosol samples collected, one-fourth portion of the filter was soaked in 50 mL of Milli-Q water (18.2 M $\Omega$  resistivity) for 4 hrs during which ultrasonication was performed in steps of 5 minutes to a total of 20 minutes to extract water soluble ionic species (WSIS). In the water extracts, inorganic anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>) ) were measured on a Dionex Ion Chromatograph [Rastogi and Sarin, 2005; Rengarajan and Sarin, 2004].



Figure 2.4: Repeat measurements of the chemical species  $SO_4^{2^-}$  (ppm) in water extract of aerosol samples.

The anions were separated on Ionpac AS14A analytical column and AG14A guard column, in conjunction with an Anion Self-Regenerating Suppressor (ASRS), using 8.0 mM Na<sub>2</sub>CO<sub>3</sub> - 1.0 mM NaHCO<sub>3</sub> as an eluent. In addition, field blanks (blank filters leached with Milli-Q water along with the aerosol samples) were also analysed and concentrations of all ionic species were corrected for procedural blanks (comprising of blank filters and analytical reagents). Typical chromatograms for anions are shown in figure 2.3. The reproducability of the sulphate measurements in the water extract of aerosol samples was assed and is shown in figure 2.4

The reason for keeping the sampling interval a constant (~ 4 hrs during the day time and ~12 hrs during the night time) was to maintain the effect of dry deposition a minimum and a constant during the course of the study so that

Month and Year	Number of Aerosol Samples Collected	Sampling Dates (Dates in corresponding Months)
September 2009	19	24, 25, 26, 27, 28, 29, 30
October 2009	16	1, 2, 3, 4, 5, 6
November 2009	24	2,3,4,5,6,7,8,9,10,11
December 2009	30	8, 9, 16, 17, 18, 19, 20, 21, 22, 23, 24
February 2010	24	12, 13, 14, 15, 16, 17, 18, 19, 20
March 2010	43	4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18

Table 2.2: Details of Aerosol Samples collected from the high-altitude remotesite Mt. Abu for the sulphate measurements

Month and Year	Number of Aerosol Samples Collected	Sampling Dates (Dates in corresponding Months)
March 2009	22	9, 10, 11, 12, 13, 15, 17, 18, 19, 20, 21, 25, 26
January 2010	56	8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31

Table 2.3: Details of Aerosol Samples collected from the high-rainfall siteShillong for the sulphate measurements

influence of other parameters such as dust content in the atmosphere, the PBL height, OH radical concentration, relative humidity (RH) etc on the molar S-ratio can be examined with more certainty. The details of the aerosol samples collected during different sampling periods for  $SO_4^{2^-}$  measurements and the molar S-ratio calculations are shown in Tables 2.2 and 2.3.

#### 2.4. Trajectory Analysis

The HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model developed by NOAA ARL [Draxler and Rolph, 2003; Rolph, 2003], was used for the present backward trajectory analysis. The HYSPLIT model uses a modeled vertical velocity scheme; it can depict the vertical motion of the relevant air parcel. The HYSPLIT computes the advection of a single pollutant particle, or simply its trajectory. Air mass back trajectory analyses for this thesis work are performed using the HYSPLIT model to investigate the source regions and the transport pathways of pollutants before they reach the measurement locations.

### 2.5. GEOS- Chem Model Description

### 2.5.1. General Description

The GEOS-Chem global 3-D model of tropospheric chemistry (v8-03-01; <u>http://acmg.seas.harvard.edu/geos/</u>) driven by GEOS-5 assimilated meteorological observations - including winds, convective mass fluxes, mixed layer depths, temperature, clouds, precipitation, and surface properties - from the NASA Global Modelling and Assimilation Office (GMAO) is employed for this work. Meteorological fields in the GEOS-5 have 6-h temporal resolution (3-hour resolution for surface fields and mixing depths) and a horizontal resolution of 0.5° latitude X 0.667° longitude, with 72 levels in the vertical extending from the surface to approximately 0.01 hPa. The model is applied to a global simulation of Ozone-NOx-VOC-aerosol chemistry. General descriptions of GEOS-Chem are given by [*Bey et al.*, 2001] and [*Park et al.*, 2004]. The detailed descriptions of the GEOS-Chem aerosol emission inventories and simulation evaluations are provided in [Park et al., 2004] and [Wang et al., 2008] for sulfur and ammonia, in [Duncan Fairlie et al., 2007] for dust, and in [Chen et al., 2009] for recent updates

on emission inventories over the China region. The simulations are conducted for Jan–Dec 2009 at 4° X 5° resolutions. They are initialized on  $1^{st}$  Jan 2009 with GEOS-Chem fields generated by a one year spin-up simulation with 4° X 5° resolution.

### 2.5.2. Emission inventories included in the model runs

In the model runs, the following emission inventories were used:

1) The EMEP - the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe - inventory for 2000 [Vestreng and Klein, 2002]

2) The Big Bend Regional Aerosol and Visibility Observational (BRAVO) inventory for 1999 [Kuhns et al., 2003]

3) The global sulphur emission based on the Emissions Database for Global Atmospheric Research (EDGAR) inventory [Olivier and Berdowski, 2001]

4) The Streets inventory [Streets et al., 2006]

5) Canada Criteria Air Contaminants (CAC) inventory for 2002 (<u>http://www.ec.gc.ca/pdb/cac/cac\_home\_e.cfm</u>) and

6) The Environmental Protection Agency (EPA/NEI05) inventory.

The various emission inventories set in the model runs is given in Table 2.4. The inventoried species in EMEP [Vestreng and Klein, 2002] - the Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe - inventory for 2000 comprise of the main pollutants SOx, NOx, NH<sub>3</sub>, NMVOC, CO from the year 1980 to 2000 as well as the particulate matter PM<sub>2.5</sub>, PM<sub>10</sub>, TSP and the heavy metals Pb, Cd, Hg / (*As, Cr, Cu, Ni, Se, Zn*).

The BRAVO inventory [Kuhns et al., 2003] has been assembled from a large number of data sources covering the 14 states in the U.S., 10 states in Mexico, and offshore platforms in the Gulf of Mexico with the emissions inventory for Mexico being the first regional scale inventory for this area. Inventoried species include CO, NH<sub>3</sub>, NOx, PM<sub>10</sub>, PM<sub>2.5</sub>, SO<sub>2</sub>, and VOC. Offshore emissions are less than 1% of the total emissions of all species with the exception of VOC's that account for ~3% of the total emissions. Emissions data

from continuous emissions monitors on major power plants in the U.S. are included in the BRAVO EI. Major emissions sources types in Mexico are similar to those in the U.S. with on and off road motor vehicles being the largest sources of CO, NOx, and VOC's in both countries. Primary particulate emissions of both  $PM_{10}$  and  $PM_{2.5}$  are due to unpaved road and paved road travel in both countries.

%%% EMISSIONS MENU %%% :	=> Use GFED2 biomass? : => monthly GFED2? : T
Turn on emissions? : T	=> 8-day GFED2? : F
Emiss timestep (min) : 60	=> 3-hr GFED2? : F
Include anthro emiss? : T	=> synoptic GFED2? : F
=> Scale 1985 to year : -1	Individual NOx sources :
=> Use EMEP emissions? : T	=> Use aircraft NOx? : T
=> Use BRAVO emissions?: T	=> Use lightning NOx? : T
=> Use EDGAR emissions?: T	=> Scale glb flrate?: T
=> Use STREETS emiss? : T	=> OTD reg redist? : F
=> Use CAC emissions? : T	=> OTD loc redist? : T
=> Use NEI2005 emiss? : T	=> Use CTH param? : T
	=> Use MFLUX param? : F
Use EPA/NEI99 (anth+bf)?: F	=> Use PRECON param?: F
w/ ICARTT modif.? : F	=> Use soil NOx : T
w/ VISTAS NOx emis? : F	=> Use fertilizer NOx : T
Include biofuel emiss? : T	NOx scaling : 1
Include biogenic emiss? : T	Use ship SO2 emissions? :
=> Use MEGAN inventory?: T	=> global EDGAR ? : T
=> Use PCEEA model? : F	=> global ICOADS ? : T
=> Use MEGAN for MONO? : T	=> EMEP over EUROPE ? : T
=> Isoprene scaling : 1	=> ship SO2 Corbett ? : F
	=> ship SO2 Arctas ? : T
Include biomass emiss? : T	Use COOKE BC/OC (N. Am.): F
=> Seasonal biomass? : T	Use AVHRR-derived LAI? : F
=> Scaled to TOMSAI? : F	Use MODIS-derived LAI? : T

Table 2.4: The various emission inventories used in the model runs. T indicatedTrue and F indicate False state for the inventory in the input. geos file

Crop tilling is the second largest emitter of PM in the U.S. In Mexico, crop tillng is not inventoried but crop burning is the second largest source of PM. Cattle husbandry is the largest source of NH<sub>3</sub> in both countries. Biogenic NH<sub>3</sub> emissions from plant respiration were not inventoried in this although estimates for the state of Texas indicate that ~50% of the total NH<sub>3</sub> may be biogenic. Both sources place the majority of NH<sub>3</sub> emissions in areas with sufficient rainfall to support forests or graze lands. SO<sub>2</sub> emissions are predominantly associated with point sources in both countries. The largest SO<sub>2</sub> source in the inventory domain is the Popocatepetl Volcano that emits ~1.4 million tons of  $SO_2$  per year (4 times larger than the next largest  $SO_2$  source). Other important  $SO_2$  sources include: the Tula industrial facility north of Mexico City; the Carbon I/II power plants south west of Big Bend; Power plants in north east Texas; and power plants in the Midwestern U.S. The inventory is integrated in to a common data format to process using the SMOKE emissions processor.

The aim of the EDGAR system [Olivier and Berdowski, 2001], which started in 1992, is to provide global anthropogenic emissions of greenhouse gases CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, HFCs, PFCs and SF<sub>6</sub> and of precursor gases CO, NOx, NMVOC and  $SO_2$ , per source category, both at country and regional scales as well as on a  $1^{\circ}x1^{\circ}$  degree Earth grid. It is made to serve as a reference database for policy applications, e.g. to provide RIVM's integrated climate change model IMAGE 2 with emissions data and for assessments of potentials for emission reductions, as well as for scientific studies by providing gridded emissions as input for atmospheric models. The EDGAR database contains estimates of emissions from many gases (see http://www.rivm.nl/edgar/). For this ISLSCP II collection gridded emission data files are provided for the total of all anthropogenic sources for 1970, 1980, 1990 and 1995 for CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O and for the precursor gases CO, NOx, NMVOC and SO<sub>2</sub> for 1990 and 1995. The files are available in their original tabular format as well as two-dimensional Earth grids. EDGAR data comprise all anthropogenic sources, including international air traffic and international shipping. These are categorised as follows

(a) Fossil-fuel production, transmission, transformation (e.g. coke production, oil refineries) and combustion

(b) Biofuel production, transformation (charcoal production) and combustion

(c) Industrial production and consumption processes (including solvent use)

(d) Agricultural activities

(e) Biomass burning

(f) Waste handling

Fossil fuel fires are included (coal fires, oil fires in Kuwait in 1992).

Parameter Definitions for this inventory are as follows:

For carbon dioxide (CO<sub>2</sub>):

- *Fuel combustion* refers to fossil fuel combustion and non-energy/feedstock use (Intergovernmental Panel on Climate Change (IPCC) category 1A) estimated using the IPCC Sectoral Approach;
- *Fugitive* refers to flaring of associated gas in oil and gas production (IPCC category 1B);
- · Industry refers to cement production (IPCC category 2); and

•*Other* refers direct emissions from tropical forest fires plus 10% of biofuel combustion emissions, which is the fraction assumed to be produced unsustainably (IPCC category

For methane (CH4):

•*Energy* comprises production, handling, transmission and combustion of fossil fuels and biofuels (IPCC category 1A and 1B);

•*Agriculture* comprises animals, animal waste, rice production, agricultural waste burning (non-energy, on-site) and savannah burning (IPCC category 4);

•*Waste* comprises landfills, wastewater treatment, human wastewater disposal and waste incineration (non-energy) (IPCC category 6);

•*Others* include industrial process emissions and tropical and temperate forest fires (IPCC categories 2 and 5).

For nitrous oxide (NO):

• *Energy* comprises combustion of fossil fuels and biofuels (IPCC category 1A and 1B);

• *Agriculture* comprises fertilizer use (synthetic and animal manure), animal waste management, agricultural waste burning (non-energy, on-site) and savannah burning (IPCC category 4);

 $\cdot$  Industrial Processes comprises non-combustion emissions from manufacturing of adipic acid and nitric acid (IPCC Source Category 2); and *others* include N<sub>2</sub>O usage, tropical and temperate forest fires, and human sewage discharge and waste incineration (non-energy) (IPCC Source Categories 3, 5 and 6)

The inventoried species in the Streets Inventory [Streets et al., 2006] include the emissions of SO<sub>2</sub>, NOx, CO, VOC,  $PM_{10}$ ,  $PM_{2.5}$ , BC, and OC by sector (power, industry, residential, and transportation) and six speciated VOCs by sector files.

The CAC (http://www.ec.gc.ca/pdb/cac/cac home e.cfm) emissions comprise oxides of nitrogen (NOx), sulphur oxides (SOx), volatile organic compounds (VOCs), carbon monoxide (CO), total particulate matter (TPM), particulate matter less than 10 microns in size (PM10), and particulate matter less than 2.5 microns in size (PM2.5). Although, not classified as a CAC, emissions of hydrogen sulphide (H2S) are also evaluated due to their recent addition to Environment Canada's National Pollutant Release Inventory (NPRI). Emissions of NO<sub>x</sub>, SO<sub>x</sub>, CO, TPM, PM<sub>10</sub> and PM<sub>2.5</sub> are attributed strictly to combustion sources. VOC and H<sub>2</sub>S emissions are attributed to venting and fugitive emissions, but are also evaluated as products of incomplete combustion. Emissions of NOx and SO<sub>x</sub> are primarily of concern as precursors to acid precipitation but are also reported to produce respiratory and other internal disease when inhaled in high concentrations and contribute to the formation of airborne PM2.5. Particulate emissions are linked to respirator problems. H<sub>2</sub>S is an air toxic as well as highly odoriferous. CO is a poisonous gas that reportedly can produce lasting health harm, mainly through its destructive effects on the central nervous system. VOCs are potentially toxic substances and are of concern as a precursor (along with NO<sub>x</sub>) to the formation of photochemical oxidants near ground level. The CAC emissions amounted to 367 kt of NOx, 265 kt of SO2, 528 kt of VOC, 766 kt of NMHC, 380 kt of CO, 9.1 kt of TPM (almost all of it PM2.5) as well as 10.3 kt of H2S. Most of the inorganic emissions are due to combustion activities. The uncertainties in the estimated total emissions of the different CACs ranged from about  $\pm 0.9$  percent to  $\pm 3.6$  percent

The National Emissions Inventory (NEI) is a comprehensive inventory covering all criteria air pollutants (CAPs) and hazardous air pollutants (HAPs) for all areas of the United States. The NEI was created by the EPA's Emission Inventory and Analysis Group (EIAG) in Research Triangle Park, North Carolina. The NEI contains emission estimates for the following CAPs:

- $\Box$  Carbon monoxide (CO)
- □ Condensable particulate matter (PM-CON)
- □ Filterable and primary particulate matter less than 2.5 microns (PM<sub>2.5</sub>-FIL and

PM<sub>2.5</sub>-PRI)

□ Filterable and primary particulate matter less than 10 microns (PM10-FIL and

PM10-PRI)

 $\Box$  Nitrogen oxides (NO<sub>x</sub>)

 $\Box$  Sulfur dioxide (SO<sub>2</sub>)

□ Volatile organic compounds (VOC)

Ammonia is also included in the NEI as a precursor to PM formation. The inventoried species in EPA includes SO<sub>2</sub>, VOC, NO<sub>x</sub>, CO, Pb, PM<sub>10</sub>, PM<sub>2.5</sub> and NH<sub>3</sub>.

2.5.3. Chemistry Mechanism

The chemical mechanism for the troposphere in the GEOS-Chem model includes 80 species and over 300 reactions with detailed photo oxidation schemes for major anthropogenic hydrocarbons and isoprene, as described by Horowitz et al. [1998]. It has been updated with recent experimental data from DeMore et al. [1997], Atkinson [1997] and Brown et al. [1999a, 1999b]. Photolysis frequencies in the troposphere are calculated using the Fast-J algorithm of Wild et al. [2000], which uses a seven-wavelength quadrature scheme and accounts accurately for Mie scattering by clouds. Surface albedo and vertically resolved cloud optical depths are taken from the GEOS meteorological archive with 6-hour resolution. The model uses climatological ozone concentrations as a function of latitude, altitude, and month to calculate the absorption of UV radiation by ozone with a recently added capacity to use ozone column information for the specific year of simulation. The chemical mass balance equations are integrated every hour using a Gear algorithm [Jacobson and Turco, 1994] for all grid boxes below the tropopause. The various Tracers available in the GEOS-Chem model for the standard run used for this thesis work is given in Table 2.5.

Natural sources of sulphur in the model include DMS from oceanic phytoplankton and  $SO_2$  from volcanoes and biomass burning. The gas-phase sulphur oxidation chemistry in the model includes DMS oxidation by OH to form

999 TDACED MENTI 999					
Type of gimulation	:	2			
Number of Tradord	:	10			
Trader Entried	:	43 TTD #	Namo	a/molo	Tragar Mambarg
() = omitted	•	IR#	Name	g/more	Iracer Members,
() = emitted		1	NOT	16 0	
IIACEI #I	•	T	NOX	40.0	NO2 (NO) NO3
HNO2		C	0	10 0	(02) NO2
IIACEI #2	•	2	ÛX	40.0	(03) NO2
ZINUS		2	TAN	101 0	
Tracer #1	:	<u>з</u>	CO	28 0	(CO)
Tracer #5	:	- 5		12 0	(CO)
Tracer #6	:	5	TGUD	12.0	( <u>+</u> C)
Tracer #7	:	0 7	TROL	63 0	( <u>UNO</u> 2 )
Tracer #8	:	γ Ω	ш0 <u>3</u>	34 0	(11105)
Tracer #9	;	a a		12 0	(3C)
Tracer #10	:	10	MER	12.0	(10)
Tracer #11	:	11		12.0	(20)
Tracer #12	:	1 2	ALDZ DCUO	12.0 58 0	(20)
$\frac{11}{2}$	:	12	MUK	70 0	
$\frac{11}{2} = \frac{11}{2} = \frac{11}{2}$	:	11	MACD	70.0	
$\frac{11}{2}$	:	15	DMN	147 0	
Tracer $\#15$	;	16	DDN	135 0	
Tracer $\#17$	:	17		110 0	
$\frac{11}{2} = \frac{11}{2} = \frac{11}{2}$	:	1.0		12 0	(3C)
Tracer $\#19$	÷	19	СЗНВ	12.0	(30)
$\frac{11}{2}$	;	20	CH20	30 0	(CH2O)
Tracer $\#21$	÷	20	C1120	12 0	(2C)
Tracer $#22$		22	N205	105 0	(20)
Tracer #23	:	23	HNO4	79 0	
Tracer #24	:	24	MP	48 0	
Tracer #25	:	25	DMS	62 0	
Tracer #26	:	2.6	S02	64.0	
Tracer #27	:	27	S04	96 0	
Tracer #28	:	2.8	S04s	96.0	
Tracer #29	:	2.9	MSA	96.0	
Tracer #30	:	30	NH3	17.0	
Tracer #31	:	31	NH4	18.0	
Tracer #32	:	32	NTT	62.0	
Tracer #33	:	33	NITS	62.0	
Tracer #34	:	34	BCPI	12.0	
Tracer #35	:	35	OCPI	12.0	
Tracer #36	:	36	BCPO	12.0	
Tracer #37	:	37	OCPO	12.0	
Tracer #38	:	38	DST1	29.0	
Tracer #39	:	39	DST2	29.0	
Tracer #40	:	40	DST3	29.0	
Tracer #41	:	41	DST4	29.0	
Tracer #42	:	42	SALA	36.0	
Tracer #43	:	43	SALC	36.0	

Table 2.5: The various Tracers in the GEOS-Chem model for the standard run

 $SO_2$  and MSA, DMS oxidation by nitrate radicals (NO<sub>3</sub>) to form  $SO_2$ , and  $SO_2$  oxidation by OH to form sulphate. Similarly the aqueous-phase oxidation chemistry in the model includes the oxidation of  $SO_2$  by  $O_3$  and  $H_2O_2$  in clouds to form sulphate.

### 2.5.4. Deposition mechanism

Dry deposition of oxidants and water soluble species in the model is computed using a resistance-in-series model based on the original formulation of Wesely [1989] with a number of Tracers for GEOS-CHEM Model Simulation of Tropospheric Ozone-NOx-Hydrocarbon Chemistry. The dry deposition velocities are calculated locally using GEOS data for surface values of momentum and sensible heat fluxes, temperature, and solar radiation. Wet deposition Includes scavenging by convective updrafts and anvils and by large-scale precipitation: this algorithm was developed by Liu et al. [2001], who evaluated it in the GEOS-CHEM by simulation of the aerosol tracer <sup>210</sup>Pb and <sup>7</sup>Be

### 2.5.5. The Model Simulation: Options set in the input.geos file

The different options which were set for the runs in the input.geos file controlling the simulation type and inputs are discussed as follows. The type of simulation was set at 3 corresponding to the global simulation of Ozone-NOx-VOC-aerosol chemistry with 43 tracers included in the runs.

In the model runs the transport menu has the following parameters set. The Transport mechanism was kept ON with a transport time step of 30 minutes. The flux correction for this menu was maintained at the default False value. In the cloud convection menu the cloud convection and PBL mixing was kept True with a convection time step of 30 minutes. The inventories, EMEP, BRAVO, EDGAR, STREETS, and NEI2005 were turned ON in the Emissions menu. The biofuel, biogenic (via MEGAN inventory) and biomass emissions were kept True during the runs. Aircraft NOx, lightning NOx, soil NOx and fertilizer NOx also were kept ON during the simulations. The ship SO<sub>2</sub> emissions were turned ON with global EDGAR, global ICOADS, EMEP over EUROPE and ship SO<sub>2</sub> Arctas maintaining at their default True values. Under the Aerosols Menu, the Sulphate,

Carbon, Online DUST, and Online SEASALT Aerosols were kept at their default True value with DEAD emissions used for the Online DUST Aerosols

```
%%% TRANSPORT MENU %%% :
                               Online DUST
                                             AEROSOLS : T
Turn on Transport : T
                                => Use DEAD emissions? : T
=> Use Flux Correction?: F
                               Online SEASALT AEROSOLS : T
=> Fill Negative Values: T
                                -- SALA radius bin [um]: 0.1
=> IORD, JORD, KORD : 3 3
                               0.5
                                -- SALC radius bin [um]: 0.5
7
Transport Timestep [min]: 30
                               4.0
Use strat O3/NOy BC's : T
                               Online dicarb. chem. : F
   ____+
%%% CONVECTION MENU %%% :
                               %%% DEPOSITION MENU %%% :
Turn on Cloud Conv?: TTurn on PBL Mixing?: T
                               Turn on Dry Deposition? : T
                     - T
- T
- T
                               Turn on Wet Deposition? : T
=> Use non-local PBL? : T
                               ----+---
Convect Timestep (min) : 30
%%% AEROSOL MENU %%%
                               %%% CHEMISTRY MENU %%% :
                     :
Online SULFATE AEROSOLS : T
                                                     : т
                               Turn on Chemistry?
                               Chemistry Timestep [min]: 60
Online CRYST/AQ AEROSOLS: F
Online CARBON AEROSOLS : T
                               Read and save CSPEC_FULL: F
Online 2dy ORG AEROSOLS : F
                               USE solver coded by KPP : T
```

Table 2.6: The various options set under the "Convection Menu", "AerosolMenu", "Deposition Menu" and "Chemistry Menu" used in the model runs. Tindicated True and F indicate False state option in the input. geos file

In the Depositions Menu both the Dry deposition and Wet deposition were kept ON. Under the Chemistry menu, the Chemistry mechanism was kept at its default True value with a Chemistry Time-step of 60 minutes. Table 2.6 shows the various options set under the "Convection Menu", "Aerosol Menu", "Deposition Menu" and "Chemistry Menu" in the input. geos file during the model runs.

### 2.5.6. Various Input Parameters to the Model:

In addition to the Emission inventories discussed previously which forms the major inputs to the model, the model uses the various input parameters from the GEOS-5 assimilated meteorological observations - including winds, convective mass fluxes, mixed layer depths, temperature, clouds, precipitation, and surface properties - from the NASA Global Modelling and Assimilation Office (GMAO) which are downloaded and fed during the model runs. Meteorological fields in the GEOS-5, as mentioned previously, have 6-h temporal resolution (3-hour resolution for surface fields and mixing depths) and a horizontal resolution of  $0.5^{\circ}$  latitude X  $0.667^{\circ}$  longitude, with 72 levels in the vertical extending from the surface to approximately 0.01 hPa. For our simulations we degrade the horizontal resolution to  $4^{0}X5^{0}$  for computational expediency.

### 2.6. GAMAP Visualization Toolkit

The Global Atmospheric Model Analysis Package (GAMAP) (Version 2.15; <u>http://acmg.seas.harvard.edu/gamap/</u>) is used for plotting the output from the GEOS-Chem runs. GAMAP is a self-contained, consistent, and user-friendly software package for reading and visualizing output from chemical tracer models (CTM's) and consists of a suite of routines written in IDL (Interactive Data Language). It can produce line plots, 2D plots, 2D animations, or 3D iso-contour surface plots and can read 2D, 3D or 4D data blocks.

### 2.7. The molar S-ratio calculation

The molar ratio of  $SO_4^{2^-}$  to total sulphur compounds ( $SO_x = SO_2 + SO_4^{2^-}$ ) termed molar S-ratio defining the formation efficiency of  $SO_4^{2^-}$  (i.e., the amount of  $SO_4^{2^-}$  produced per  $SO_2$  emitted from the emission sources) is calculated for the sampling periods for our sampling sites of Mt. Abu and Shillong as follows. The sulphate ( $SO_4^{2^-}$ ) accumulated in the aerosol samples collected during each sampling interval is measured using an ion chromatograph. The median of the SO<sub>2</sub> concentrations recorded during the same sampling interval also is calculated from the 5 min data downloaded from the SO<sub>2</sub> analyzer. The molar S-ratio is then calculated using the above obtained SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> concentrations for same sampling interval, and the mean/median of the molar S-ratios obtained for the sampling month is taken as a representative figure for the SO<sub>2</sub> oxidation efficiency of the atmosphere for the sampling month for the sampling site.

### Chapter 3

## Spatio-temporal trends in the ambient SO<sub>2</sub> levels: High rain fall versus semi-arid region

### Introduction

Asian region is fast evolving as one of the major energy consuming regions in the world for a rapidly growing population and emerging economy. [Guttikunda et al., 2003], projected mega cities in Asia as one of the large emission sources of SO<sub>2</sub>. As per IPCC 2007, there has been a regional shift in the emissions of SO<sub>2</sub> from US and Europe to South-East Asia, with implication to shift in atmospheric radiative forcing patterns for these regions [Boucher and Pham, 2002; Pham et al., 2005; Smith et al., 2004]. With the objective of understanding the spatio-temporal variability in the ambient SO<sub>2</sub> concentrations over the Indian region, measurements were performed from three sites namely Shillong, Mt. Abu and Ahmedabad having different characteristic features as is discussed in Chapter 2. The results are discussed in this chapter and the observations are explained on the basis of back trajectory analysis performed using HYSPLIT as well as on the basis of the results generated using the chemical trasport model GEOS-Chem.

# **3.1 Effect of Asian dust storms on the ambient SO<sub>2</sub> concentration over north-east India: A case study**

### **3.1.1. Introduction**

Monitoring ambient  $SO_2$  concentration coupled with wind trajectory analysis in the North-East region of India - characterized by high rain fall - has special significance to assessing the role of long range transport from North-East Asia in controlling the pollutant characteristics over this region. With this objective, ambient  $SO_2$  concentrations were measured during March 2009 and January 2010 at a high rainfall site in North-East India, Shillong (25.67<sup>0</sup> N, 91.91<sup>0</sup> E, 1064 m Above Sea Level (ASL))

### **3.1.2. Results and Discussions:**

Using pulsed UV fluorescence analyzer, the ambient SO<sub>2</sub> concentrations were measured at the high rainfall site, Shillong  $(25.67^{0} \text{ N}, 91.91^{0} \text{ E}, 1064 \text{ m ASL})$  in North-East India, during March 2009 and January 2010. During the measurements the inlet of the SO<sub>2</sub> analyzer was maintained at an altitude of about 15m above the ground, while the analyzer was housed in an air conditioned room. The integration time for the analyzer was set at 5 minutes. An Automated Weather Station (AWS) located within a distance of  $\frac{1}{2}$  km from the sampling site was employed to monitor the various atmospheric parameters such as the wind speed, wind direction, relative humidity, atmospheric pressure etc, throughout the sampling period.

### 3.1.2.1. Major Features during March 2009

Figure 3.1.1 reveals the temporal changes of the SO<sub>2</sub> concentrations at Shillong, during March 2009. The concentration levels recorded during the initial days of the sampling were very high (Max: 262.3 ppbv) which decayed down gradually towards the end the sampling period. This observed high SO<sub>2</sub> concentrations is explained as due to a transient long range pollutant transport from North-East Asia associated with the cold air outbreak preceding the dust storm events reported in China [Li and Song, 2009] on 14<sup>th</sup> March 2009 and in North–East India [Sharma et al., 2010] on 17<sup>th</sup> March 2009. The former [20], using MODIS 1B data of relevant regions, showed evidences for the dust storm in western Gansu and Neimenggu in China while the latter [21], based on Terra/Aqua MODIS data, reported the dust storm over Guwahati, North-East India. Based on the mesoscale model (MM5) derived wind speed directions at 850 hPa overlaid on sea level pressure on 17<sup>th</sup> March 2009, [*Sharma et al.*, 2010] found a persistent North-Easterly flow with high wind speed (~6 m/s) over the region resulting in mobilization and lifting of dust particles in to the atmosphere.

They analyzed NCEP temperature/relative humidity (RH) anomalies variations and found ~ $0.6^{0}$  C increase in surface air temperature and ~ -4% reduction in RH during March 2009, which they said has resulted in dry conditions over the region. They attributed the very high value of Terra MODIS AOD<sub>550</sub> (~1.3) along with lower value of Alpha ( $\sim 0.78$ ) to coarse mode dust aerosol particles over the region due to dust event occurred on  $17^{\text{th}}$  March 2009.



Figure 3.1.1: The measured  $SO_2$  time series profile during March 2009 at the sampling site, Shillong.

The above argument of long range transport as the mechanism responsible for the observed high SO<sub>2</sub> values at the North-East Indian sampling site is based on the results provided collectively by the back trajectory analysis performed using HYSPLIT for the sampling period and the model runs performed using the Chemical Transport Model GEOS-Chem. The arguments are further supported with the local meteorological parameters measured using nearby Automated Weather Station (AWS). The time series Mineral Dust Optical Depth (MOPD) profiles created using GEOS-Chem (discussed in the following sections) for the month of March 2009 also gave evidence for the dust storm movement reported in China on 14<sup>th</sup> March 2009.

## 3.1.2.1.1. Interpreting the High SO<sub>2</sub> Values3.1.2.1.1.1 Source Identification Based on HYSPLIT Trajectories:

The 7 day back trajectories beginning from the sampling site were generated (figure 3.1.2) using HYSPLIT for whole the sampling month, with one

trajectory plot made each on 1<sup>st</sup>, 8<sup>th</sup>, 15<sup>th</sup>, 22<sup>nd</sup> and 29<sup>th</sup> of March 2009. The trajectories computed to identify the source regions were for altitudes 500m, 1000m and 4000m Above Ground Level (AGL). The plots showed clearly that between 8<sup>th</sup> and 15<sup>th</sup> of March 2009 there was a drastic change in wind trajectories. During this period the winds which were travelling in the eastward direction suddenly got bend and started travelling towards North-East till it reach ~  $60^0$  N and from there it again got bend and started travelling towards the south to reach the sampling site. It was in line with this observed sudden change in the wind trajectory (between 8<sup>th</sup> and 15<sup>th</sup> of March 2009), the high SO<sub>2</sub> concentrations were recorded. The back trajectories plotted for the following weeks again showed wind patterns similar to the ones persisted prior 8<sup>th</sup> March 2009. The observed decay in concentration levels during the days succeeding the transient long range pollutant transport were in line with this normal trajectory pattern.

### 3.1.2.1.1.2 Source Identification Using GEOS-Chem Model

The GEOS-Chem model (v8-03-01) was run from  $1^{st}$  January 2009 to  $31^{st}$ December 2009, after spinning up the model fields for one year, and the output averaged for the first half of each month was generated. The results were then plotted using GAMAP to find out the possible SO<sub>2</sub> source regions along the back trajectories obtained between 8<sup>th</sup> and 15<sup>th</sup> of March 2009.







# Figure 3.1.2: The 7-day back trajectories originating at the sampling site plotted using HYSPLIT for March 2009

The plots clearly showed that many of the regions over which the winds travelled during this period are characterized by high concentrations of  $SO_2$ . Out of these the Perm region in Russia has the highest  $SO_2$  concentration in the GEOS-Chem generated plots.

### 3.1.2.1.1.2.1 The Perm City, Russia

Perm, projected in this paper as the source region for the high  $SO_2$  containing air parcel detected at the sampling site, is a city in the eastern part of Russia, near the Urals Mountains. It is a major center of heavy industries, chemical industries (varnishes, paints, fertilizers, sulfuric acid, etc.), petrochemical and oil refining industries, defense production, timber and wood processing industries, food industry and so on. This regional area has substantial deposits of natural resources (oil, gas, potassium, magnesium salt, precious and jobbing stones, gold and chromium ores and so on.) which is the base for both the extractive industries and related economic sectors of the region. The region of Perm has one of the richest mineral resource bases in Russia and has many mines.

The Perm region is known for its long frosty, snowy Ural winters. However, the region's severe continental climate causes abrupt seasonal changes, from a cold winter followed by a mild, usually warm spring and then by a hot summer. The cold winter necessitates central heating especially during the months Nov, Dec, Jan, Feb, and Mar. The general precipitation trend over Perm region shows lowest precipitation events during the months February and March followed by slightly higher precipitation events in April.

### 3.1.2.1.1.3. Anomalies Detected in Local Meteorology

The Automated Weather Station (AWS) - located within 500m from the sampling location - provided meteorological parameters such as wind speed & wind direction (figure 3.1.3), relative humidity (figure 3.1.4) and atmospheric pressure (figure 3.1.5) throughout the month of March 2009 except for a small non-operational period from 20 - 23<sup>rd</sup> March 2009. Statistically the wind direction mostly remained South-East with second directional preference for South-West. The wind speed showed a transient increase between 9<sup>th</sup> and 13<sup>th</sup> of March 2009 with the maximum speed recorded of 3.2 m/s. The relative humidity (RH) remained more or less on the higher side throughout the sampling period with a small dip recorded between 10<sup>th</sup> and 12<sup>th</sup> followed by two spikes each on 13<sup>th</sup> and 14<sup>th</sup>. The highest RH value observed for the month was on 17<sup>th</sup> with the peak relative humidity value recorded of 99%.



Figure 3.1.3: Wind speed and wind direction during the sampling period, obtained from nearby AWS



Figure 3.1.4: Relative humidity during the sampling period, obtained from nearby AWS



Figure 3.1.5: Atmospheric pressure during the sampling period, obtained from nearby AWS

The Atmospheric pressure also kept unusually fluctuating with a dip observed between  $3^{rd}$  and  $7^{th}$  (lowest value 891 hPa) and a hump observed between  $12^{th}$  and  $15^{th}$  of March 2009 (Max value 903.3 hPa).

### 3.1.2.1.1.4. Dust Storm Detection Using GEOS-Chem

To visualize and understand the source and the trajectory of the dust storms reported [*Li and Song*, 2009] in China on 14<sup>th</sup> March 2009 and over North-East India [*Sharma et al.*, 2010] on 17<sup>th</sup> March 2009, the GEOS-Chem model was run with the inventories discussed previously, and generated the time series Mineral Dust Optical Depth (MOPD) data for the month of March 2009. The plots generated from these data for the days 10<sup>th</sup> to 20<sup>th</sup> of March 2009 (figure 3.1.6) clearly showed this formation and the movement of the dust storm. The plots also showed high MOPD values for the Indo-Gangetic Plane also during 13<sup>th</sup> and 14<sup>th</sup> March 2009. A second phase of high MOPD values for North-East India started on 17<sup>th</sup> March 2009 which remained high in the following few days (18<sup>th</sup> , 19<sup>th</sup> and 20<sup>th</sup> March 2009).









Figure 3.1.6: The Mineral Dust Optical Depth (MOPD) profile (unitless) obtained during 10<sup>th</sup> to 20<sup>th</sup> of March 2009 from GEOS-Chem.

### 3.1.2.1.1.4.1 Cold Air Outbreaks and Dust Storms in Asia

It is known that Asian dust storms, especially those of Chinese origin occur during spring [Liu, 1985], when the climate over East Asia reaches its maximum dryness of the year, the surface start warming, and strong winds sweep over the desert areas leading to highly unstable synoptic systems. The percentages of dust storms generally occurring in China during March, April, and May are 20%, 58%, and 22%, respectively [Sun et al., 2001].





# Figure 3.1.7: The Trajectory Matrix plotted using HYSPLIT for the cold air out break period

Asian dust storms are always associated with cold air outbreaks, resulting in the Mongolian cyclonic depression and frontal system. It is known that polar front causes mid-latitude jet stream (by the thermal wind relationship) with troughs and ridges to lead to patterns of divergence aloft. This upper air disturbance causes a significant pressure decrease in the lower atmosphere as a result of cyclogenesis, leading to the development of a low pressure system with low central sea level pressures which continue to deepen as time progress to cause cyclone and a resulting dust mobilization.

The reason the sampling was planned during this season at this North-Eastern Indian site was to understand the possible effects of such cold air outbreaks and the associated atmospheric disturbance preceding the Chinese dust storms in altering the atmospheric pollutant transport pattern to North-East India.

To visualize this air disturbance associated with the cold air outbreak occurred during the above sampling period, trajectory matrices were plotted on 8<sup>th</sup>, 11<sup>th</sup>, 15<sup>th</sup>, 22<sup>nd</sup> and 29<sup>th</sup> of March 2009 with source at multiple locations (figure

3.1.7). The plots clearly indicated a major atmospheric disturbance between 8<sup>th</sup> and 15<sup>th</sup> of March 2009.

3.1.2.1.2. Transport from Russian Region: Implication to the Asian Pollutant Outflow

The observation that  $SO_2$  got transported from the highly industrialized areas of Perm in Russia to North-East India during the dust storm event in March 2009 has important implications to its share in the Asian pollutant outflow to the Pacific during spring, every year. To make this picture clear, 7 day back trajectories starting at co-ordinates ( $18^0$  N,  $130^0$  E) and ( $22^0$  N,  $110^0$  E), (figure 3.1.8) were plotted which showed the air parcel from Russian region reaching the Pacific during the dust storm days. Based on these observations, it is projected here that the contribution from this region is non negligible while assessing the impact of Asian pollutant outflow, as the Perm region is characterized by a wide range of industries.



Figure 3.1.8: The 7- day back trajectories showing the air parcel from Russian region reaching the Pacific during the dust storm events

The GEOS-Chem generated  $SO_2$  plots for every month (averaged over the first 15 days) plotted for the whole year 2009 (figure 3.1.9) clearly showed the tropospheric  $SO_2$  over Perm region peaking during Nov, Dec, Jan, Feb and Mar every year, possibly because of central heating. The lesser amount of precipitation in the Perm region during the months February and March result in longer atmospheric retention time for these pollutants during these months. The concentration levels go decreasing when there is increase in precipitation events starting from April along with the receding winter to reduce the central heating requirements.

























Figure 3.1.9: SO<sub>2</sub> profile averaged for the first half of every month for 2009 from GEOS-Chem model runs showing the SO<sub>2</sub> peaking over the Perm region in Russia, during the months Nov, Dec, Jan, Feb and Mar.

The model runs were also performed to find out the concentration levels of other major pollutants over this region during March 2009. It was found that regions in and around Russia has relatively high concentrations of atmospheric NOx, Peroxyacetyl Nitrate (PAN), Lumped Peroxypropionyl Nitrate (PPN), HNO<sub>3</sub>, HNO<sub>4</sub>,  $C_3H_8$ ,  $C_2H_6$ , SO<sub>4</sub>, NH<sub>4</sub>, Inorganic Sulphur Nitrates (NIT), and Lumped Alkyl Nitrate (R<sub>4</sub>N<sub>2</sub>) (figure 3.1.10).






















Figure 3.1.10: NOx, Peroxyacetyl Nitrate (PAN), Lumped Peroxypropionyl Nitrate (PPN), HNO<sub>3</sub>, HNO<sub>4</sub>,  $C_3H_8$ ,  $C_2H_6$ , SO<sub>4</sub>, NH<sub>4</sub>, Inorganic Sulphur Nitrates (NIT) and Lumped Alkyl Nitrate ( $R_4N_2$ ) profiles averaged for the first half of March 2009 from GEOS-Chem model runs.

The model runs also showed (figures not included here) that similar to  $SO_2$ , these pollutants also peak during Nov, Dec, Jan, Feb, and Mar every year, again possibly has association with central heating and climatology discussed above. But the fact that cold air outbreaks preceding the dust storm events in Asia occur only during March, April and May makes the relative contribution from this region significant only during March, when the atmospheric pollutant peak for the region overlaps with the dust storm months (March, April, May).











Figure 3.1.11:  $N_2O_5$ ,  $NH_3$ , hydrophilic black carbon (BCPI), hydrophilic organic carbon (OCPI), hydrophobic black carbon (BCPO), hydrophobic organic carbon (OCPO) profiles averaged for the first half of March 2009 from GEOS-Chem model runs.

So it suggest that during the dust storm events in March, the contribution from regions in and around Russia may not be neglected while considering the impact of Asian pollutant outflow to the Pacific, which becomes less significant during cold air outbreaks and the associated dust storms happening in April, and May. The model runs also showed (figure 3.1.11) that the pollutants  $N_2O_5$ ,  $NH_3$ , hydrophilic black carbon, hydrophilic organic carbon, hydrophobic black carbon and hydrophobic organic carbon are present only in smaller levels in the Perm region compared to the other known polluted regions in North East Asia, and so are not expected to contribute significantly to the Asian pollutant outflow.

#### 3.1.2.2. SO<sub>2</sub> Time-Series Data (March 2009): Model Versus Observations:

Figure 3.1.12 shows the time series  $SO_2$  profile obtained for the nearest coordinates ( $26^0$  N,  $90^0$  E) from the GEOS-Chem model runs for the month of March 2009. The model was not able to pick up the magnitude of this major transport event even though a slight increase in the  $SO_2$  levels were observed between  $8^{th}$ and  $16^{th}$  of March 2009 and in general the concentrations resembled more or less to the background levels expected for this high rainfall site in the absence of long range transports.

#### 3.1.2.3. Major Features during January 2010

Unlike March 2009 the  $SO_2$  concentrations recorded during January 2010 (figure 3.1.13) were well within the acceptable limits, with maximum value going up to 29.7 ppbv only and a minimum value recorded of 1.94 ppbv. The wind back trajectory analysis (figure 3.1.14) showed that the winds were coming from West Asian region and had no component coming from North-East Asia ruling out the possibility of any long range transport from Russia.

So the concentration levels recorded may be taken as the back ground  $SO_2$  values for this North-Eastern Indian site.

#### 3.1.2.4. SO<sub>2</sub> Time-Series Data (January 2010): Model Versus Observations:

In the case of January 2010, the time series output from the model (figure 3.1.15) matched more or less with the observations both magnitude wise and to certain extend shape wise. The diurnal variation observed in the experimental data is reproduced in the model generated time series output.



Figure 3.1.12: SO<sub>2</sub> time series profile generated using GEOS-Chem for the sampling period in March 2009 for the nearest co-ordinates  $(26^{\circ} N, 90^{\circ} E)$ 



Figure 3.1.13: The measured  $SO_2$  time series profile during January 2010 at the sampling site, Shillong.



Figure 3.1.14: The 7-day back trajectories originating at the sampling site plotted using HYSPLIT for January 2010



Figure 3.1.15: SO<sub>2</sub> time series profile generated using GEOS-Chem for the sampling period in January 2010 for the nearest co-ordinates  $(26^{\circ} N, 90^{\circ} E)$ 

## 3.1.3. Conclusions

Ambient SO<sub>2</sub> concentrations at Shillong (25.67<sup>o</sup>N, 91.91<sup>o</sup>E, 1064 m ASL), a high rain fall site located in North East India, measured during March 2009 and January 2010 showed significant differences in magnitude, with concentrations going to a maximum of 262.3 ppbv during the former sampling period - which decayed down gradually towards the end the sampling period - against the maximum value recorded during the latter period of 29.7 ppbv. This elevated SO<sub>2</sub> concentrations during March 2009 is explained as due to a long range transport associated with the cold air outbreak preceding one of the dust storm events reported in China. This argument of long range transport for the observed high SO<sub>2</sub> values during March 2009 is formulated on the basis of the back trajectory analysis performed using HYSPLIT for the sampling period - the plots clearly showed a drastic change in wind trajectories between 8<sup>th</sup> and 15<sup>th</sup> of March 2009 wherein the winds travelled over some of the highly polluted regions such as the Perm region of Russia - and on the basis of the results from simulations performed using the global 3-D model of tropospheric chemistry, GEOS-Chem (v8-03-01) – it clearly showed the tropospheric SO<sub>2</sub> over Perm region peaking during Nov, Dec, Jan, Feb and Mar every year, possibly due to central heating.

The observation of long range transport of  $SO_2$  from the highly industrialized areas of Perm in Russia to North-East India during the dust storm event in March 2009 is projected to have important implications to its share in the Asian pollutant outflow to the Pacific during spring, every year. Separate runs of the model revealed that the regions in and around Russia have high concentrations of other atmospheric pollutants such as NOx, Peroxyacetyl Nitrate, HNO<sub>3</sub>, Lumped Peroxypropionyl Nitrate, HNO<sub>3</sub>, HNO<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>2</sub>H<sub>6</sub>, SO<sub>4</sub>, NH<sub>4</sub>, Inorganic Sulphur Nitrates and Lumped Alkyl Nitrate. The model runs also showed that some of the other atmospheric pollutants such as N<sub>2</sub>O<sub>5</sub>, NH<sub>3</sub>, hydrophilic black carbon, hydrophilic organic carbon, hydrophobic black carbon and hydrophobic organic carbon are present only in negligible levels in the Perm region compared to the other polluted regions in North-East Asia and so will not contribute significantly to the Asian pollutant outflow.

The comparison of the time series  $SO_2$  profile obtained for the nearest coordinates (26<sup>0</sup> N, 90<sup>0</sup> E) from the GEOS-Chem model with the experimental data, for the month of March 2009, revealed that the model was not able to pick up the magnitude of this transport whereas there is a good correlation between the two for January 2010.

# **3.2.** Ambient SO<sub>2</sub> concentration over a high altitude site in semiarid Western India: Seasonal variability

### 3.2.1. Introduction

Monitoring sulphur gases in the free troposphere is important to understand their effects on the global climate because of the multi-roles they play in the chemistry of global troposphere and in the biogeochemical sulphur cycle [e.g., Cullis and Ilirschler, 1980; Rodhe and Isaksen, 1980; Freney et al., 1983; Toon et al., 1987; Saltzman and Cooper, 1988; Bates et al.,1987, 1990; Andreae, 1990; Andreae and Jaeschke, 1992]. With this objective, a high altitude remote site, Gurushikhar, Mt. Abu ( $24.6^{0}$  N 72.7<sup>0</sup>E, 1680 m asl) with a more or less clean and stable atmosphere was selected. The Gurushikhar site has the special characteristics of occasional accommodation within the free troposphere as function of season making it quite suitable for the kind of study reported here. In addition, during favourable wind conditions, periodic long range transport of pollutants to Gurushikhar occurs, offering the opportunity to study the effect of long range transport in controlling the ambient  $SO_2$  levels over this relatively pristine site.

#### **3.2.2. Results and Discussions**

SO<sub>2</sub> concentrations were measured from the semi arid high altitude site, Mt. Abu, during the months Feb '09, Sept '09, Oct '09, Nov '09, Dec '09, Feb '10 and Mar '10 with the aim to understand the seasonal variability in the ambient SO<sub>2</sub> levels over this semi-arid high altitude site. The GEOS-Chem Chemical Transport Model is used to generate the SO<sub>2</sub> profile for the Indian region for the sampling months which helped identifying the major SO<sub>2</sub> source regions. Now by analysing the back trajectories generated using HYSPLIT for the sampling periods – performed at different altitudes to investigate the source and the transport pathways of pollutants before they reach the measurement locations - and correlating them with the GEOS-Chem generated SO<sub>2</sub> plots showing the SO<sub>2</sub> source regions, the observed peaks and troughs in the measured SO<sub>2</sub> spectrum is explained in the following sections.

#### 3.2.2.1. SO<sub>2</sub> Plots for different Months

The GEOS-Chem model runs were performed with the inventories discussed in Chapter 2, to find out the major source regions of SO<sub>2</sub> in India and its seasonal variability. The output averaged for the first half of each month was then plotted using GAMAP and is shown in figure 3.2.1 for different months of the year 2009. The plots showed the region around co-ordinates  $30^{0}$  N and  $75^{0}$  E with very high concentrations of SO<sub>2</sub> throughout the year. The sampling site Mt. Abu is only a few co-ordinates away from this source region and hence can act as a source for the long range transport of SO<sub>2</sub> to the sampling site depending on the origin of the wind back trajectories - and hence a season dependent





Figure 3.2.1:  $SO_2$  concentration (ppbv) over the Indian region averaged for the first half of each month of the year 2009 showing the major source regions, generated using the GEOS-Chem model.

long range transport contribution, including the free tropospheric transport due to the high elevation of the site, to the ambient  $SO_2$  levels - and is discussed in the following sections, taking the case of each sampling period.

#### 3.2.2.2. SO<sub>2</sub> Measurements at Mt. Abu

Ambient  $SO_2$  measurements were made at Mt Abu during the sampling periods span over the months Feb '09, Sept - Oct '09, Nov '09, Dec '09, Feb '10, and Mar '10. The time series profiles had distinctly different features during different sampling periods, which has association with the transport patterns and the climatology prevailed on that particular month as is discussed in the following sections. The major features observed during each sampling month and its correlation with various atmospheric parameters is discussed below.

#### 3.2.2.1 Major Features: February 2009

During February '09 when the wind back trajectories (shown in figure 3.2.2) extended to regions located around co-ordinates  $30^0$  N and  $75^0$  E lying North and North-East of the sampling site, a region projected as the one with highest SO<sub>2</sub> concentration in India in the GEOS – Chem generated plots (figure 3.2.1), the time series profile has many spikes with a mean concentration of 4.3 ppbv and a standard deviation of 0.792 ppbv.

The spikes in the spectrum (figure 3.2.3) were found to be positively correlating with the arrival of air parcel from the high SO<sub>2</sub> region around the coordinates  $30^0$  N and  $75^0$  E, emphasizing the prominent role of long range transport in controlling the ambient SO<sub>2</sub> levels over this high altitude remote site under the climatic conditions prevailing here in month of February The SO<sub>2</sub> profile showed some sort of a diurnal variation pattern (figure 3.2.4) with the minimum concentration values reported between 0700 hrs and 1000 hrs IST. This dip in concentration may be explained as due to a sudden rise in the planetary boundary layer height (as is explained in Chapter 5, based on GEOS- Chem model calculations) and a consequent dilution of the SO<sub>2</sub> concentration at the ground level as well as the rapid increase in the OH radical concentration - which increases the SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> conversion rate. Both the PBL height and the OH radical carrying the



Figure 3.2.2: The wind back trajectories plotted for various days during the sampling period in Feb '09 generated using HYSPLIT.



Figure 3.2.3: The time series SO<sub>2</sub> profile recorded during the sampling period in February 2009, at Mt. Abu



Figure 3.2.4: The diurnal pattern for the SO<sub>2</sub> concentration measured during the sampling period in February 2009 at Mt.Abu

concentration are known to correlate positively with the incoming solar radiation (INSOLATION). The possible diurnal variability in the wind patterns  $SO_2$ 

containing air parcel to the sampling site also could be a reason for the observed diurnal pattern in the  $SO_2$  values.

#### 3.2.2.2.2. Major Features: September – October 2009

During Sept - Oct '09, when the winds were mostly from the South-West direction (as shown in figure 3.2.5), originating mostly from Arabian Sea where  $SO_2$  concentration is a minimum in the GEOS-Chem generated plots, the  $SO_2$  concentration measured at Mt. Abu showed a near constant value with very few spikes (figure 3.2.6).

The mean and standard deviation of the concentration values obtained during the sampling period are 4.3 ppbv and 0.21 ppbv respectively. The spikes in the spectrum observed on the  $2^{nd}$  and  $3^{rd}$  of Oct '09 correlate very well with a change in trajectory pattern when the winds from the high SO<sub>2</sub> source region around the co-ordinates,  $30^{0}$  N and  $75^{0}$  E (figure 3.2.1) carried high SO<sub>2</sub> containing air parcel to the sampling site.

Also the SO<sub>2</sub> profile had little diurnal variability (figure 3.2.7) which is explained as due to the very high OH radical concentration present during these months for a higher water vapour content and insolation rate – the two parameters necessary for the production of OH radical in the atmosphere via photo chemistry. The high enough OH radical concentration possibly makes sure sufficient oxidation for SO<sub>2</sub> even when the PBL height is low (as is shown in Chapter 5), nullifying the PBL height variation effects and hence the non observation of the diurnal variability.

The very negligible contribution from long range transport – as almost all the back trajectories originated from the low  $SO_2$  regions over Arabian Sea - and hence the non dependence of the  $SO_2$  concentration on any possible diurnality of the wind pattern, also could be a reason for the minimum disturbance observed in  $SO_2$  time series profile.





Figure 3.2.5: The wind back trajectories plotted for various days during the sampling period in Sept-Oct '09 generated using HYSPLIT.



Days (Sept-Oct 2009)

Figure 3.2.6: The SO<sub>2</sub> time series spectrum recorded during the sampling period in Sept-Oct '09 at Mt. Abu



Figure 3.2.7: The diurnal pattern for the SO<sub>2</sub> concentration measured during the sampling period in Sept-Oct 2009 at Mt. Abu

#### 3.2.2.3. Major Features: November 2009

During Nov '09 when the wind back trajectories (figure 3.2.8) extended mostly to North - East, the SO<sub>2</sub> profile showed short duration spikes superimposed on the back ground values. The mean and standard deviation of the SO<sub>2</sub> values recorded (figure 3.2.9) during the sampling period are 3.4 ppbv and 1.25 ppbv respectively.



Figure 3.2.8: The wind back trajectories plotted for various days during the sampling period in Nov '09 generated using HYSPLIT.



Figure 3.2.9: The SO<sub>2</sub> time series spectrum recorded during the sampling period in Nov '09 at Mt. Abu



# Figure 3.2.10: The diurnal pattern for the SO<sub>2</sub> concentration measured during the sampling period in November 2009 at Mt. Abu

The long range transport may be contributing to the  $SO_2$  concentration recorded in Nov '09 as the back trajectories showed pollutant transport from the high  $SO_2$  region in the GEOS-Chem generated plots located around  $30^0$  N and  $75^0$  E as well

as low  $SO_2$  source regions in the GEOS-Chem generated maps for the Indian region (eg., regions lying in the North – East part of the sampling site) for November '09.

Because of the wind pattern specific for this month, only short duration random air parcels from the high SO<sub>2</sub> regions around  $30^{0}$  N and  $75^{0}$  E arrive at the sampling site at Mt. Abu - as shown by the back trajectory analysis (figure 3.2.8) - explaining the observed short duration spikes in the measured SO<sub>2</sub> profile against the more broader spikes observed in Feb '09.

A diurnal pattern is observed (Figure 3.2.10) in the measured  $SO_2$  profile, which may be attributed to the combined effects put in by the insolation dependent variation in OH radical levels and PBL height as well as the diurnal variation in the wind pattern carrying pollutants to the sampling site from long distances.

The spikes as well as the concentration values decreased from  $12^{\text{th}}$  Nov '09 which has association with the trajectory change from high SO<sub>2</sub> regions around  $30^{0}$  N and  $75^{0}$  E to relatively lower SO<sub>2</sub> regions lying in the North – East part of the sampling site.

#### *3.2.2.3.1.* Detection of SO<sub>2</sub> plume from a major Oil fire incident:

A major fire had broken out at one of the oil storage tanks, holding 8,000 kilolitres (280,000 cu ft) of oil, at the Indian Oil Corporation's (IOC) oil depot, in Sitapura Industrial Area on the outskirts of Jaipur, Rajasthan (26.92°N 75.82°E) on 29<sup>th</sup> October 2009 at around 7:30 PM (IST). The fire broke out when the oil was being transferred from the depot to a pipeline.

The huge ball of fire with loud explosion engulfed the leaking petrol tank which slowly spread to other nearby petrol tanks with continuous fire with flames rising 30–35 m (98–115 ft) and was visible even from a 30 km (19 mi) distances. Almost 60,000 kilolitres (2,100,000 cu ft) of oil in 11 storage tanks went up in flames on the evening of Oct 29 and the blaze raged till Nov 6. The blaze remained out of control for more than a week forcing the evacuation of half a million people from the area to safer places (*fire incident details courtesy: Wikipedia*)

The Meteorological department recorded a tremor measuring 2.3 on the Richter scale during the first explosion event which resulted in shattering of glass window nearly 3 kilometres from the accident site. The air pollution levels over the region in and around Jaipur went way above maximum permitted limits and affected the visibility conditions of the region.



Figure 3.2.11: The wind back trajectories plotted for plume transport days in Nov '09 generated using HYSPLIT

The Central Pollution Control Board's (CPCB) assessment showed evidences for the significant effects this pollution episode had on the air in Delhi and Agra.

We measured the SO<sub>2</sub> levels over this high altitude site, Mt. Abu to study the possible long range transport of plumes from the disaster site at Jaipur. There were three short duration high magnitude spikes recorded (figure 3.2.12) each on  $2^{nd}$  (around 0125 hrs) 4<sup>th</sup> (around 2230 hrs) and 5<sup>th</sup> (around 2120 hrs) of Nov '09 which has association with the major fire erupted at an IOC depot in Jaipur as the back trajectories showed air parcels reaching the sampling site from co- ordinates surrounding 26.9°N and 75.8°E, during the above days (figure 3.2.11).



Figure 3.2.12: The SO<sub>2</sub> spikes detected at Mt. Abu when plumes from the Jaipur Oil fire site (26.92<sup>•</sup>N 75.82<sup>•</sup>E) reached the sampling site

3.2.2.2.4. Major Features: December 2009

During Dec '09, the winds were mostly coming (as seen in the back trajectory plots shown in figure 3.2.13) from North and North-East carrying high SO<sub>2</sub> from the source regions located around co-ordinates  $30^{0}$  N and  $75^{0}$  E – the region projected as the strongest SO<sub>2</sub> source region in India in the GEOS – Chem

generated plots (figure 3.2.1) resulting in the elevated  $SO_2$  concentration values at the sampling site (figure 3.2.14) with many spikes. The mean  $SO_2$  value and the standard deviation recorded during this sampling period are 3.5 ppbv and 1.28 ppbv respectively.



Figure 3.2.13: The wind back trajectories plotted for various days during the sampling period in December '09 generated using HYSPLIT.



Figure 3.2.14: The  $SO_2$  time series spectrum recorded during the sampling period in December '09 at Mt. Abu



Figure 3.2.15: The diurnal pattern for the SO<sub>2</sub> concentration measured during the sampling period in December '09 at Mt. Abu

The observation of a shift in concentration values from higher during the initial sampling days to relatively lower towards the end of the sampling period is

explained by the shift in the wind back trajectory pattern from high  $SO_2$  source regions to low  $SO_2$  regions lying in the eastern side.

A diurnal pattern is observed during this sampling period (figure 3.2.15) with the minimum value at around 1000 hrs IST, which is explained as due to the combined effect of PBL height variation and OH radical concentration variability. A possible periodic variation in the wind pattern carrying polluted air to the sampling site from long distances also could be a reason for the observed variability, as indicated by more number of ups and downs than can be explained by OH and PBL variability.

The GEOS – Chem based calculations showed that it is in the month of December every year, the contribution of long range transported  $SO_2$  over Mt. Abu attains its maximum peak as will be discussed in the following sections.

#### 3.2.2.5. Major Features: February 2010

The sampling period in Feb '10 was characterized by higher  $SO_2$  values (figure 3.2.16) and clear diurnal variability. The sampling period saw high  $SO_2$  values during the initial sampling period followed by a dip and the concentration again rose towards the end of the sampling period.



Figure 3.2.16: The SO<sub>2</sub> time series spectrum recorded during the sampling period in February 2010 at Mt. Abu

This is well explained by comparing the backward wind trajectories (figure 3.2.17) during the sampling periods with the GEOS-Chem generated  $SO_2$  profiles (figure 3.2.1).





Figure 3.2.17: The wind back trajectories plotted for various days during the sampling period in February 2010 generated using HYSPLIT.

During the initial days of sampling all three components of the wind trajectories (plotted for altitudes 50m, 500 m and 3000 m) extended to the high SO<sub>2</sub> regions in the GEOS-Chem generated plots (figure 3.2.1), located around the co- ordinates  $30^{0}$  N and  $75^{0}$  E. But during the time when dip in SO<sub>2</sub> values where observed, the only trajectory at 50 m altitude carried pollutants from the high SO<sub>2</sub> region around  $30^{0}$  N and  $75^{0}$  E whereas the higher altitude trajectories (at 500 m and 3000 m) came from the West Asian region where no major hot spots of SO<sub>2</sub> prevailed as per GEOS- Chem results.

The fact that the Mt. Abu sampling site enters the free tropospheric zone during the winter time further explain the non-influence of pollutant carrying winds in the lower lying layers of the atmosphere on the ambient  $SO_2$  levels during this month.

The mean SO<sub>2</sub> concentration and the standard deviation recorded during the sampling period are 7.73 ppbv and 1.45 ppbv respectively. Strong diurnal pattern was observed during this sampling period (figure 3.2.18) which is attributed to the large diurnal PBL height variation as seen in the GEOS – Chem model generated PBL values for this month, discussed in the following sections.



Figure 3.2.18: The diurnal pattern for the SO<sub>2</sub> concentration measured during the sampling period in February 2010 at Mt. Abu

#### 3.2.2.2.6. Major Features: March 2010

During the sampling period in Mar '10 also, high SO<sub>2</sub> concentrations were recorded (figure 3.2.19). Occasional long range transport of SO<sub>2</sub> to the sampling site is indicated by the back trajectory analysis which showed (figure 3.2.20) arrival of air parcel from both the high SO<sub>2</sub> regions around  $30^0$  N and  $75^0$  E and from low SO<sub>2</sub> regions such as the Arabian sea and West Asia. The mean SO<sub>2</sub> concentration and the standard deviations recorded during this sampling period are 9.19 ppbv and 2.4 ppbv respectively. A well defined diurnal variability pattern (figure 3.2.21) is a characteristic feature for this period, which is attributed to the very large diurnal variability in the PBL heights as shown in the GEOS – Chem generated time series PBL values, discussed in the following sections. The diurnal pattern resembled the one observed in Feb '10 with the whole graph shifted by ~ 3 hrs to the left along the time axis. This shift is explained as due to the increase in the insolation rate from February to March at this high altitude site, to cause the PBL height increase to take place in the morning hours itself compared to February.



Figure 3.2.19: The  $SO_2$  time series spectrum recorded during the sampling period in March 2010 at Mt. Abu



Possible diurnal variation in the wind pattern carrying polluted air to the sampling site also could be another reason for the diurnal SO<sub>2</sub> variability.

Figure 3.2.20: The wind back trajectories plotted for various days during the sampling period in March 2010 generated using HYSPLIT.



Figure 3.2.21: The diurnal pattern for the SO<sub>2</sub> concentration measured during the sampling period in March 2010 at Mt. Abu

3.2.2.3. Explaining the Diurnal Variations in SO<sub>2</sub> Conc. using GEOS-Chem Model

The diurnality pattern observed in the measured  $SO_2$  profile over Mt. Abu as well as those in the GEOS-Chem generated  $SO_2$  time series data for different months of the year 2009 (shown in Figure 3.2.22) is explained based on the time series PBL height and OH radical values generated using the GEOS-Chem model runs in the following sections. The diurnal pattern observed for PBL height and OH radical concentration for different months of the year 2009, seen in the time series data generated using the GEOS-Chem model are shown in figure 3.3.23 and figure 3.2.24 respectively.

The GEOS-Chem generated  $SO_2$  profiles (figure 3.2.22) showed that during Jan, Feb, Mar, April and May there is a sudden dip in the  $SO_2$  concentration values between 0600 hrs and 0800 hrs IST.

This may be explained on the basis of the diurnality pattern seen in the time series PBL heights (figure 3.2.23) as well as OH radical concentration profiles (figure 3.2.24) generated using GEOS – Chem. During the above months (Jan, Feb, Mar, April and May), the PBL height remain below 100m during night time till 0600 hrs IST followed by a 10 - 20 fold increase in PBL height by 0800 hrs, which

continue to rise till 1400 hrs, remain more or less constant till 1600 hrs, followed by a decrease in its value to reach the minimum value by 2000 hrs IST and continue to remain at this minima till 0600 hrs IST. The spread in the values increases from the Jan to Jun with the maximum spread observed in the month of June, followed by a decrease.









Figure 3.2.22: The diurnality pattern observed in the GEOS-Chem generated  $SO_2$  time series data for the co-ordinates ( $26^0N$ ,  $75^0E$ ) different months of the year 2009

The minimum diurnal variability in the PBL heights were observed during July to Sept. A close look at the diurnal pattern of OH radical for the year 2009 generated using GEOS – Chem showed highest OH radical concentrations during the months, Jun, Jul, Aug, and Sept followed by a decrease till December and then the accenting mode for OH radical levels in the atmosphere start from January. Unlike the diurnality pattern observed for the PBL heights, where during the months of Jan – May there is a transient increase in the values between 0600 hrs and 0800 hrs, the OH variation during the above months are at a relatively slow pace.



#### Chapter - 3



Figure 3.2.23: The diurnality pattern observed in the GEOS-Chem generated PBL height data for the co-ordinates  $(26^{\circ}N, 75^{\circ}E)$  for different months of the year 2009

The sudden manifold increase in OH values between 0600 hrs and 0800 hrs IST takes place during the months May, Jun, July when the relative humidity (RH) in the atmosphere is sufficiently high over this region. The minimum OH radical concentrations were recorded during the month of December when both the insolation as well the atmospheric water content – the two major

parameters controlling the OH formation in the atmosphere - are on the lower side. The OH radical concentrations as well as the PBL heights for different months of the year 2009 obtained from the GEOS-Chem model are shown in figures 3.2.25 and 3.2.26 respectively.













Figure 3.2.24: The diurnality pattern observed in the GEOS-Chem generated OH radical concentrations (molecules/cm<sup>3</sup>) data for the co-ordinates ( $26^{0}N$ ,  $75^{0}E$ ) for different months of the year 2009

As can be seen in these figures the PBL height maximum and OH radical concentration maximum doesn't overlap but falls on different months to give a season dependent variation in the relative contributions to the  $SO_2$  conversion efficiency and is discussed in detail in the following sections.


Figure 3.2.25: OH radical concentration (molecules/cm<sup>3</sup>) during different months of the year 2009 over  $(26^{\circ}N, 75^{\circ}E)$  generated using GEOS-Chem



Figure 3.2.26: PBL heights (m) during different months of the year 2009 over  $(26^{0}N, 75^{0}E)$  generated using GEOS-Chem

3000

3500

4000

2e+6

1e+6

## 3.2.2.3.1. Relative contribution of PBL height and OH radical conc. on the $SO_2$ levels

It is evident from the above discussion that the interplay between seasonal PBL height and the OH concentration variability are major factors controlling the diurnality pattern of the SO<sub>2</sub> concentrations. The fact that the rate at which these two parameters vary - both seasonal as well as diurnal variation - are different leads to a season dependent diurnality pattern for SO<sub>2</sub>.

During the months Feb, Mar, April the effect put in by the sudden change in PBL height in the morning hours leads to the sudden decrease in the SO<sub>2</sub> values between 0600 hrs and 0800 hrs IST, where the OH radical variation is not sufficient to cause much changes in this pattern. Whereas the sudden changes in the OH concentrations occurring during the months Jun – Sept is the major player in controlling the SO<sub>2</sub> diurnality pattern during these months.



PBL Height (m) 1500

2500

3000

3500

OH CONC (NUMber density)

2e+6

1e+6



GEOS - Jul '09









GEOS - Oct '09





Figure 3.2.27: Three dimensional graphs showing the  $SO_2$  concentration dependence on the OH radical levels (molecules/cm<sup>3</sup>) and PBL heights (m) for different months of the year 2009. The time series  $SO_2$ , OH and PBL heights were obtained from the GEOS-Chem model.

To visualize the above mentioned relative contributions clearly, 3dimensional graphs were plotted with the GEOS–Chem generated OH concentration along X – axis, PBL height along Y – axis and the SO<sub>2</sub> concentration along the Z – axis for different months of the year 2009 (figure 3.2.27). During all the months, the SO<sub>2</sub> concentration was found to be decreasing with PBL height as well as the OH radical concentration. During the month of January, a PBL height variation from near zero to 600m takes the SO<sub>2</sub> value to a constant for all the OH values lying above  $2e^{+6}$ . Similarly even with the highest OH concentration available with the month (~7e<sup>+6</sup>), the SO<sub>2</sub> concentration is not pulled down for PBL values below ~ 400m. The random peaks observed in the SO<sub>2</sub> values for January has got to do with other parameters controlling the SO<sub>2</sub> concentration over the region, and the transient long range transport is one possible player.

During Feb '09, for all values of OH concentration above  $4e^{+6}$ , an increase in PBL height above ~ 700 m is sufficient to pull the SO<sub>2</sub> values to the minimum for that month. Below an OH level of ~  $4e^{+6}$ , a combined effect of OH radical as well as PBL height variation is found to influence the SO<sub>2</sub> concentration. Similarly for OH concentrations below  $2e^{+6}$ , even with the highest PBL height recorded for the month, the SO<sub>2</sub> concentration remained high. Compared to Jan '09, the graph plotted for Feb '09 has few uncorrelated humps in  $SO_2$  values, indicating the possible shift in the transport pattern from Jan to Feb over the sampling region.

The graph for the month of March '09 shows clearly the interplay between the PBL and OH values in controlling the SO<sub>2</sub> concentration. This is one such month were both PBL values as well as OH concentration are significant. As a result, for OH values between  $1e^{+6}$  and  $4e^{+6}$ , the increase in PBL height from the minimum of the month to 1500 m, SO<sub>2</sub> concentration decreased at a steady rate to reach the minimum SO<sub>2</sub> levels for the month. For all OH values above  $4e^{+6}$ , the SO<sub>2</sub> concentration drops to the minimum value for PBL heights above ~ 700 m. Interference from other players such as transient long range transport is a minimum in this month as evidenced by the absence of any random humps in the SO<sub>2</sub> values.

The behaviour observed in April, May and June were somewhat similar to the one in March. The scenario started changing from July and became clearly visible by August, when the OH concentration in the atmosphere reached its peak values of the year. In August, the OH concentration was sufficient to pull down the SO<sub>2</sub> values to the minimum of the month for all PBL values above ~ 150 m, showing the major role the OH radical play in controlling the ambient SO<sub>2</sub> concentration for this month. The non - observation of any humps in the SO<sub>2</sub> values correlate very much with the minimum transient transport expected for these months, underlining our argument that the third major player controlling the ambient SO<sub>2</sub> levels over this region is the long range transport.

During Sept '09 and Oct '09, when the boundary layer heights are on the lower side, the OH radical and transport are the only major players resulting in many humps in the  $SO_2$  values in addition to the contribution from heterogeneous phase oxidation on water. During Nov and Dec, when an overlap of low PBL heights with low OH concentration along with higher transport events keep the  $SO_2$  values on the higher side during most of the time as seen in the 3 dimensional graphs.

## 3.2.2.4. Effect of long range transport on ambient SO<sub>2</sub> levels over Mt. Abu

In order to understand the possible effects of long range transport of  $SO_2$  on the measured  $SO_2$  values over Mt. Abu, GEOS-Chem model runs were performed with all the parameters keeping identical to the previous full input runs but now with the Transport mechanism turned OFF. Now the percentage difference in the  $SO_2$  concentration over the sampling site (nearest co-ordinates in the GEOS-Chem model ( $26^{0}N$ ,  $75^{0}E$ )) in the absence of transport is calculated as follows:

Percent Difference in the SO<sub>2</sub> concentration in the absence of Transport = (WithOutTransport – FullInput)\*100/FullInput

where :

## WithOutTransport $\rightarrow$ SO<sub>2</sub> concentration recorded when the Transport turned OFF

## FullInput $\rightarrow$ SO<sub>2</sub> concentration recorded when all parameters were ON

Figure 3.2.28 shows the percent difference in the  $SO_2$  concentration over the co-ordinates (26<sup>0</sup>N, 75<sup>0</sup>E) in the absence of the transport mechanism. In this case sources located within the 4<sup>0</sup>X5<sup>0</sup> grid containing the Mt. Abu site only contribute to the observed SO<sub>2</sub> levels. It is found that in the absence of transport, there in a decrease in the SO<sub>2</sub> levels for all the months of the year, but with varying magnitude.



Figure 3.2.28: Percent Difference in the SO<sub>2</sub> concentration in the absence of Transport for different months of the year 2009 calculated using GEOS- Chem model runs for the co-ordinates (26<sup>0</sup>N, 75<sup>0</sup>E).





Figure 3.2.29: The time series percent decrease in the  $SO_2$  levels in the absence of the transport mechanism for different months of the year 2009.

The months Jan, Feb, Mar, and April receives the minimum contribution from long range transport while the months July and December sees the highest long range contribution to the ambient  $SO_2$  levels. The rest of the months have intermediate values for the long range transport contribution. Figure 3.2.29 shows the time series percent decrease in the  $SO_2$  levels in the absence of the transport mechanism for different months of the year 2009.

#### **3.2.3. Summary and Conclusion:**

The ambient  $SO_2$  concentrations were measured from the semi arid high altitude site, Mt. Abu, during the months Feb '09, Sept '09, Oct '09, Nov '09, Dec '09, Feb '10 and Mar '10 with the aim to understand the seasonal variability in  $SO_2$  levels over this semi-arid high altitude site. The GEOS-Chem Chemical Transport Model is used to generate the  $SO_2$  profile for the Indian region for the sampling months which helped identifying the major  $SO_2$  source regions. Now by analysing the back trajectories generated using HYSPLIT for the sampling periods – performed at different altitudes to investigate the source and the transport pathways of pollutants before they reach the measurement locations - and correlating them with the GEOS-Chem generated  $SO_2$  plots showing the  $SO_2$  source regions, the observed peaks in the measured  $SO_2$  spectrum is explained.

During February '09 when the wind back trajectories extended to regions located around co-ordinates  $30^{0}$  N and  $75^{0}$  E lying North and North-East of the sampling site, the time series profile has many spikes with a mean concentration of 4.3 ppbv and a standard deviation of 0.792 ppbv, emphasizing the prominent role of long range transport in controlling the ambient SO<sub>2</sub> levels over this high altitude remote site under the climatic conditions prevailing here in the month of February.

During Sept - Oct '09, when the winds originated mostly from Arabian Sea the SO<sub>2</sub> concentration measured at Mt. Abu showed a near constant value with very few spikes – which correlated with a change in trajectory pattern when long range transport from high SO<sub>2</sub> source region around the co-ordinates,  $30^0$  N and  $75^0$  occurred. The absence of diurnal variability during this period is explained as due to the very high OH radical concentration present during these months for a higher water vapour content and insolation rate.

During the sampling period in November 2009, the back trajectories showed pollutant transport from the high SO<sub>2</sub> region located around  $30^0$  N and  $75^0$  E as well as low SO<sub>2</sub> source regions, in the GEOS-Chem generated plots for the Indian region. During this sampling period, three short duration high magnitude spikes were recorded each on  $2^{nd}$  (around 0125 hrs)  $4^{th}$  (around 2230 hrs) and  $5^{th}$  (around 2120 hrs) of Nov '09 which has association with a major oil fire erupted at an IOC depot in Jaipur as the back trajectories showed air parcels reaching the sampling site from co- ordinates surrounding 26.9°N and 75.8°E, during the above days. During Dec '09, the winds were mostly from North and North-East carrying high SO<sub>2</sub> from the source regions located around co-ordinates  $30^0$  N and  $75^0$  E which resulted in the elevated SO<sub>2</sub> concentration values at the sampling site with many spikes and had a mean and standard deviation recorded of 3.5 ppbv and 1.28 ppbv respectively.

The sampling period in Feb '10 saw higher  $SO_2$  values and a clear diurnal variability. High  $SO_2$  values were recorded during the initial sampling period followed by a dip and the concentration again rose towards the end of the sampling period. The Strong diurnal pattern observed during this sampling period is attributed to the large diurnal PBL height variation. During the sampling period in Mar '10 also, high  $SO_2$  concentrations were recorded with a mean and standard deviation recorded of 9.19 ppbv and 2.4 ppbv respectively. A well defined diurnal variability pattern is a characteristic feature for this period, which is attributed to the very large diurnal variability in the PBL heights.

The diurnality pattern observed in the measured  $SO_2$  profile over Mt. Abu for different months of the year 2009 can be explained based on the time series PBL height and OH radical values generated using the GEOS-Chem model runs. The GEOS-Chem generated  $SO_2$  profiles showed that during Jan, Feb, Mar, April and May there is a sudden dip in the  $SO_2$  concentration values between 0600 hrs and 0800 hrs IST which is explained on the basis of the diurnality pattern seen in the time series PBL heights as well as OH radical concentration profiles generated using GEOS – Chem.

A study using the GEOS-Chem model, aimed at understanding the possible effects of long range transport on the measured  $SO_2$  values over Mt. Abu showed that there is a decrease in the  $SO_2$  levels in the absence of transport during all the months of the year, but with varying magnitude.

## 3.3. Ambient SO<sub>2</sub> concentration over an urban site (Ahmedabad) in Western India

## **3.3.1. Introduction**

Ambient  $SO_2$  measurements over a semi-arid urban site Ahmedabad with numerous industrial establishments and two coal burning thermal power plants in the vicinity were performed during Apr '10, May '10, Jul '10, Aug '10 and Sept '10 with the aim to understand the characteristic features of  $SO_2$  spectra over a source region in comparison to the remote sites devoid of any local sources. The results are discussed in the following sections.

## 3.3.2. Major Features: April 2010

Ambient SO<sub>2</sub> Concentrations measured during April 2010 at the sampling site in Ahmedabad showed random spikes superimposed on a near continuum (figure 3.3.1). The mean SO<sub>2</sub> concentration and the standard deviation recorded during this sampling period are 33.13 ppbv and 22.23 ppbv respectively.



Figure 3.3.1: The SO<sub>2</sub> time series spectrum recorded during the sampling period in April 2010 at Ahmedabad

Some sort of diurnality pattern (figure 3.3.2) was observed for this sampling period, which didn't appear to be to due to the PBL height or OH radical concentration variation but can be attributed to the diurnal variation in the wind pattern carrying polluted air from the nearby thermal power plants and industrial establishments located in the vicinity of few kilometres.

As may be seen in the trajectory matrix shown in figure 3.3.3, the wind direction is mostly from the west where there are no major sources of  $SO_2$  in the



Figure 3.3.2: The diurnal pattern for the SO<sub>2</sub> concentration measured during the sampling period in April 2010 at Ahmedabad



Figure 3.3.3: The back trajectory matrix plotted for 15<sup>th</sup> of April 2010 for the sampling region

GEOS-Chem generated plots (as seen previously), the contribution from long range transport on the observed  $SO_2$  levels for this month over this urban site may be taken to be negligible, and the observed  $SO_2$  is mostly from local sources.

The relatively higher SO<sub>2</sub> levels for this month may be explained by a higher coal burning rate in the two thermal power plants situated in the northeast at a distance of about 10 km (Sabarmati:~350 MW per day) and 25 km (Gandhi Nagar: 700 MW per day) to meet the power requirement over this region during this summer month.

## 3.3.3. Major Features: May 2010

The SO<sub>2</sub> time series recorded during the sampling period in May 2010 is shown in figure 3.3.4. The concentrations were high during the initial days of sampling which decreased in magnitude towards the end of the sampling month. The mean and the standard deviation for the sampling period are 26.99 ppbv and 10.76 ppbv respectively. The time series data didn't show any noticeable diurnality (figure 3.3.5) but the spread in values were found to be a minimum between 1600 hrs and 1900 hrs probability has association with the diurnality in the wind pattern carrying polluted air to the sampling site.



Figure 3.3.4: The SO<sub>2</sub> time series spectrum recorded during the sampling period in May 2010 at Ahmedabad



Figure 3.3.5: The diurnal pattern for the SO<sub>2</sub> concentration measured during the sampling period in May 2010 at Ahmedabad



Figure 3.3.6: The back trajectory matrix plotted for 15<sup>th</sup> of May 2010 for the sampling region

Unlike the high altitude Mt. Abu site, the PBL variation doesn't appear to affect the SO<sub>2</sub> concentration levels over this lower altitude urban site in this month.

The trajectory matrix shown in figure 3.3.6 indicated air parcel arriving at the sampling site from west and travelling towards the North-East direction. For this month also the long range transport is expected to play only minor roles compared to local emissions as there are no major source regions in the GEOS – Chem plots as seen previously, beneath the back trajectories. Similar to the sampling period in April, the month of May also recorded higher SO<sub>2</sub> values which may be attributed to the higher emissions associated with the enhanced power production rate in the nearby coal burning thermal power plants during this summer month.

### 3.3.4. Major Features: July 2010

Figure 3.3.7 shows the time-series  $SO_2$  profile obtained during July 2010. This month, which sees the initiation of raining events over the sampling region, recorded a mean  $SO_2$  concentration of 25.63 ppbv and a standard deviation of 5.63 ppbv. As can be seen in figure 3.3.8 the diurnal variability was nil for this month and the spread in the values were near constant during different hours of the day.



Figure 3.3.7: The SO<sub>2</sub> time series spectrum recorded during the sampling period in July 2010 at Ahmedabad



Figure 3.3.8: The diurnal pattern for the  $SO_2$  concentration measured during the sampling period in July 2010 at Ahmedabad



Figure 3.3.9: The back trajectory matrix plotted for 15<sup>th</sup> of July 2010 for the sampling region

The trajectory matrix shown in figure 3.3.9 indicated the wind arrival to the sampling site from the Arabian Sea where there is no sources of  $SO_2$ , as per the

GEOS – Chem generated  $SO_2$  plots discussed earlier. The decrease in the power requirement in the month of July, when the rain events start over the sampling region explains the observed reduction in the  $SO_2$  concentration values for this month. The removal of atmospheric  $SO_2$  via washout also help decrease the  $SO_2$  levels over the sampling site.

## 3.3.5. Major Features: August 2010

The time series  $SO_2$  profile recorded during Aug 2010 is shown in figure 3.3.10. The mean and the standard deviation recorded for this month are 19.15 ppbv and 3.4 ppbv respectively. Similar to the previous month, any observable diurnal variability was absent in this month also for the  $SO_2$  concentration as is seen in figure 3.3.11.



Figure 3.3.10: The  $SO_2$  time series spectrum recorded during the sampling period in August 2010 at Ahmedabad

For the month of August the back trajectories originated in the Arabian Sea (figure 3.3.12) with the air parcel moving in the northeast direction. For this month also the contribution from long range transport is expected to be a minimum as there are no  $SO_2$  sources below the back trajectories. The lower power production rate also contributes to the observed lower  $SO_2$  levels in this month.



Figure 3.3.11: The diurnal pattern for the  $SO_2$  concentration measured during the sampling period in August 2010 at Ahmedabad



Figure 3.3.12: The back trajectory matrix plotted for 15<sup>th</sup> of August 2010 for the sampling region

## 3.3.6. Major Features: September 2010



Figure 3.3.13: The SO<sub>2</sub> time series spectrum recorded during the sampling period in September 2010 at Ahmedabad



Figure 3.3.14: The diurnal pattern for the  $SO_2$  concentration measured during the sampling period in September 2010 at Ahmedabad

Figure 3.3.13 shows the time series  $SO_2$  profile recorded for the month of September 2010. The mean and the standard deviation recorded for this sampling period are 14.7 ppbv and 2.3 ppbv respectively. As is shown in figure 3.3.14 no diurnal variability was recorded for this period and the spread in  $SO_2$  values were minimum for this sampling period.

In this month, the back trajectories (figure 3.3.15) originated in the Arabian Sea and travelled toward the eastward direction after reaching the sampling region. In this case also the long range transported  $SO_2$  is a minimum over the sampling site and the lower emission rate from the nearby coal burning thermal power plants leads to the observed low  $SO_2$  levels compared to the other sampling months.



Figure 3.3.15: The back trajectory matrix plotted for 15<sup>th</sup> of September 2010 for the sampling region

## 3.3.7: Summary and Conclusion:

The ambient  $SO_2$  measurements over the semi-arid urban site Ahmedabad with numerous industrial establishments and two coal burning thermal power plants in the vicinity were performed during the months, Apr '10, May '10, Jul '10, Aug '10 and Sept '10 to understand the characteristic features of SO<sub>2</sub> spectra over source regions as compared to the remote sites devoid of any local sources.

During April 2010 the  $SO_2$  time series data showed random spikes superimposed on a near constant continuum with a mean  $SO_2$  concentration recorded of 33.13 ppbv and a standard deviation of 22.23 ppbv.

The SO<sub>2</sub> time series recorded during the sampling period in May 2010 showed high concentration values during the initial days of sampling which decreased in magnitude towards the end of the sampling month. The mean and the standard deviation for the sampling period are 26.99 ppbv and 10.76 ppbv respectively with no noticeable diurnality.

Similarly, the time-series  $SO_2$  profile obtained during July 2010, which sees the initiation of raining events over the sampling region, recorded a mean  $SO_2$ concentration of 25.63 ppbv and a standard deviation of 5.63 ppbv. The diurnal variability was nil for this month and the spread in the values were near constant during different hours of the day.

During Aug 2010 the time series  $SO_2$  profile recorded a mean and standard deviation of 19.15 ppbv and 3.4 ppbv respectively. The contribution from long range transport is expected to be a minimum for this month as there are no  $SO_2$  sources below the back trajectories - extending mostly to the Arabian Sea.

The sampling period in September 2010 recorded a mean  $SO_2$  concentration and standard deviation of 14.7 ppbv and 2.3 ppbv respectively. No diurnal variability was recorded for this period and the spread in  $SO_2$  values were a minimum. The back trajectories originated in the Arabian Sea and travelled toward the east after reaching the sampling region and hence the long range transported  $SO_2$  is a minimum over the sampling site for this month.

## Chapter 4

## The SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> conversion efficiency of the atmosphere under various environmental conditions:

## 4.1. Introduction

Aerosol sulphate is produced in the atmosphere predominantly by the oxidation of its precursor species SO<sub>2</sub> emitted directly to the atmosphere via fossil fuel combustion, industrial processes and volcanic eruptions. Atmospheric oxidation of SO<sub>2</sub> occurs via both heterogeneous and homogeneous pathways. Earlier studies (Hidy et al., 1978; Husar and Patterson, 1980) of the spatiotemporal variability of SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> point to the fact that the molar ratio of sulphate to total sulphur compounds (SO<sub>x</sub> = SO<sub>2</sub> + SO<sub>4</sub><sup>2-</sup>), termed S-ratio, show a seasonal dependence. (Kaneyasu et al., 1995), showed that the S-ratio can be used as measure of the formation efficiency of SO<sub>4</sub><sup>2-</sup>. This chapter presents a study aimed at assessing the temporal and spatial variability in the sulphur conversion ratio (S-ratio).

Although a number of studies of sulfur chemistry exists (Hewitt, 2001; Hidy et al., 1978; Husar and Patterson, 1980), a comparative study aiming at understanding differences in the formation efficiency of  $SO_4^{2-}$  between sites characterized by long range advective transport and located at high elevation with those at a high rainfall site is still lacking. The sulfur chemistry at a remote location devoid of localized sources and having a constant  $SO_2$  background will be different from those at a high rainfall site. In tandem with this idea, the molar S-ratios were calculated during different months over two sites Mt. Abu – a remote high altitude site with occasional long range transport of pollutants and Shilling – a high rainfall site in North East India.

## 4.2. Results and Discussions

#### 4.2.1. The molar S-ratios at Mt. Abu

At Mt. Abu simultaneous measurements of  $SO_2$  and  $SO_4^{2-}$  were made during the months, September '09, October '09, November '09, December '09, February '10 and March '10.

The molar ratio of  $SO_4^{2^-}$  to total sulphur compounds ( $SO_x = SO_2 + SO_4^{2^-}$ ) termed molar S-ratio defining the formation efficiency of  $SO_4^{2^-}$  (i.e., the amount of  $SO_4^{2^-}$  produced per  $SO_2$  emitted from the emission sources) was calculated for the above sampling periods for our sampling site at Mt. Abu. For this the sulphate ( $SO_4^{2^-}$ ) accumulated in the aerosol samples collected during each sampling interval was measured using an ion chromatograph. The median  $SO_2$  concentration during the same sampling interval also was calculated from the 5 min data downloaded from the  $SO_2$  analyzer. Then the average molar S-ratio for that month - a representative of the oxidation efficiency of the atmosphere for the sampling month for that sampling site - is obtained by taking the mean/median of the molar S-ratio values obtained for each sampling interval.

The mean and median of the molar S-ratio values obtained during different sampling months at Mt. Abu are given in table 4.1.

During the summer months Feb '10 and March '10 the S-ratios were lower compared to the winter months Nov '09 and Dec '09. Intermediate values between these two were recorded during the sampling months Sept '09 and Oct '09, with slightly higher values for the former compared to the latter. The lower Sratios during the summer months Feb '10 and Mar '10 may be explained by the higher PBL heights compared to the other sampling months and the resulting dilution of SO<sub>2</sub> in the lower layers of the atmosphere to reduce the SO<sub>2</sub> loss from the atmosphere via dry deposition.

A detailed discussion on the PBL effect on molar S-ratio is given in Chapter 5, based on GEOS-Chem model study. An increase in the mean free path of the molecules due to higher PBL height – resulting from a decrease in the molecular density - also may have resulted in lesser number of collisions between the OH radicals and SO<sub>2</sub> molecules to result in lower conversion efficiencies.



Figure 4.1: Experimentally obtained molar S-ratios during different sampling periods at Mt. Abu showing its temporal variability.

Similarly the lower water vapor – a precursor for the OH radical formation in the atmosphere via photo chemistry - content in the atmosphere during the summer months lead to lower concentrations of OH radical to lower the atmospheric oxidation efficiency of  $SO_2$ .

Lower relative humilities (RH) during the summer months also reduce the chances of heterogeneous phase oxidation on water droplets, lowering the molar S-ratio values further. Even though some of the favorable conditions such as the relatively higher dust load in the atmosphere exist during these summer months – due to its semi-arid nature – compared to the other sampling months, offering the possibility of heterogeneous phase oxidation on dust surfaces to raise the molar S-ratio values, as is discussed in Chapter 5, the effect seems to be insufficient to bring up the molar S-ratio values to the extent that the above discussed negating effects are compensated.

Also the possibility of an enhancement in the oxidation efficiency due to longer retention time of  $SO_2$  – as suggested by Miyakawa *et al.*, 2007 - because of

a higher PBL height and the resulting reduced loss due to dry deposition, didn't help compensate the molar S-ratio decline. Similarly the possibility of the less contribution from long range transport, as discussed in Chapter 3, and hence the absence of aged air masses during these months could be another reason for the observed low molar S-ratio values during Feb '10 and Mar '10.

	Mt. Abu site	
Sampling Month	Mean molar S-ratio	Median molar S-ratio
September 2009	0.16	0.15
October 2009	0.12	0.10
November 2009	0.30	0.29
December 2009	0.29	0.28
February 2010	0.11	0.10
March 2010	0.09	0.08

## Table: 4.1: The mean and median of the molar S-ratio values obtained experimentally over Mt. Abu during different sampling periods.

The PBL heights during the months November and December are among the lowest of the year – as will be shown from the GEOS-Chem model results in Chapter 5 - leading to a higher loss rate of  $SO_2$  to the ground via the dry deposition – as the  $SO_2$  molecular density near the ground are high under low PBL conditions – and hence a high molar S-ratio. As is discussed in Chapter 2, the contribution from long range transport to the  $SO_2$  concentration at the sampling site at Mt. Abu is highest during the months November and December, leading to the presence of aged air masses over the sampling site which result in a higher molar S-ratio (But in this case the molar S-ratio needs to be dealt with caution as it is also an indicative of air mass ageing in addition to a measure of the conversion efficiency). The relative humidity also is on the higher side during these months leading to significant contributions from heterogeneous phase oxidation on water droplets to enhance the molar S-ratio values. It appeared that the negative feed-back to the molar S-ratio due to the relatively lower OH radical concentration during these months - as shown in Chapter 5 - compared to the rest of the year didn't help pull down the molar S-ratio values.

During the months September and October when the molar S-ratios showed intermediate values lying between the summer months (Feb and March here) and the winter months (Nov and Dec here), it is presumable that the molar S-ratios get both positive and negative feed backs from the parameters such as the PBL height, OH radical concentration, Relative Humidity and transport of aged air mass. For example during these months, the PBL heights are lower than those for the months of February and March causing a more efficient removal of SO<sub>2</sub> via dry deposition as discussed previously to cause a higher molar S-ratio than these months. Similarly the PBL values for September is less – as is shown in Chapter 5 - than that for the month of October resulting in more amount of SO<sub>2</sub> getting lost via dry deposition to lead to a higher molar S-ratio for September compared to October. As will be discussed in Chapter 5, the relative humidity for September is higher compared to October to cause a higher conversion efficiency and the molar S-ratio, via heterogeneous phase chemistry. Regarding the effect of long range transport, the months September and October sees less SO<sub>2</sub> contribution from long range transport compared to December and hence a lower S-ratio

# 4.2.1.1. The SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> variability over Mt. Abu: Major Observations 4.2.1.1.1. September 2009

Figure 4.2 shows the  $SO_4^{2-}$  concentration and the median of the  $SO_2$  concentrations measured in each sampling interval for the sampling period in Sept '09 from which the molar S-ratios were calculated.

A prominent observation is that both  $SO_2$  and  $SO_4^{2-}$  variations are in phase with each other but with varying magnitudinal difference. During the initial sampling days of this month, the  $SO_4^{2-}$  variability was found to be pronounced

Chapter - 4

compared to the  $SO_2$  variability when compared to the rest of the sampling days where the difference in the  $SO_2$  and  $SO_4^{2-}$  variabilities are relatively lower in magnitude.



Figure 4.2: The  $SO_4^{2^2}$  and median of the  $SO_2$  concentrations recorded during each sampling interval for the sampling period in September 2009 over Mt. Abu showing its systematic variation

This may either be explained as due to a more favorable oxidizing conditions for  $SO_2$  over the sampling site during the initial sampling days or be explained as due to a difference in the source regions for  $SO_2$  from which the long range transport to the sampling site occurred – for example it may be a more aged air mass reaching the sampling site during the initial sampling days compared to rest to cause higher conversion of  $SO_2$  to  $SO_4^{2-}$  and hence the observed higher  $SO_4^{2-}$  content during the initial days.

## 4.2.1.1.2. October 2009

In the case of October '09 (figure 4.3), both  $SO_2$  and  $SO_4^{2-}$  variabilities were in phase during different sampling intervals. The relative difference in the magnitude for  $SO_2$  and  $SO_4^{2-}$  were more or less the same throughout the sampling periods, indicative of the uniformity in the oxidizing conditions prevailing over the sampling site during this month as well as the transport patterns.



Figure 4.3: The  $SO_4^{2^2}$  and median of the  $SO_2$  concentrations recorded during each sampling interval for the sampling period in October 2009 over Mt. Abu showing its systematic variation

4.2.1.1.3. November 2009

During the sampling period in November 09, when a major oil fire erupted at a site located few co-ordinates away (as is discussed in Chapter 3), the SO<sub>2</sub> and  $SO_4^{2-}$  variability (figure 4.4) showed some very interesting trends. During the initial days of sampling both the SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> variabilities were in phase with

each other which slowly started moving out of phase and almost 180 degree out of phase in the second half of the sampling period.

This may be explained as follows. The major oil fire erupted at Jaipur  $(26.92^{\circ}N 75.82^{\circ}E)$  caused a large amount of SO<sub>2</sub> plume in the atmosphere which remained there for more than a week. During the initial days of the sampling only the SO<sub>2</sub> got transported to the sampling location at Mt. Abu because of the higher mobility of gas molecules compared to particulate matter. During the second half of the sampling period the SO<sub>4</sub><sup>2-</sup> produced over the disaster region via oxidation of the huge amount of SO<sub>2</sub> emitted during the oil fire started reaching the sampling location to give higher SO<sub>4</sub><sup>2-</sup> concentrations even when the SO<sub>2</sub> over the sampling location is low.



Mean Time and Date of Sampling

Figure 4.4: The  $SO_4^{2-}$  and median of the  $SO_2$  concentrations recorded during each sampling interval for the sampling period in November 2009 over Mt. Abu showing its systematic variation

The other possible explanation is that the fire incident ate away a huge amount of OH radicals – the major oxidizing species in the atmosphere – which resulted in reduction in the oxidation efficiency of the atmosphere at least during the night time. The insolation dependent OH radical production caused some OH production during the day time to enhance the SO<sub>2</sub> oxidation process during day time to give the high SO<sub>4</sub><sup>2-</sup> values during day time as is the case in the second half of the sampling period. The result is: During day time because of the increase in PBL height, the SO<sub>2</sub> concentration decreases but the SO<sub>4</sub><sup>2-</sup> concentration increases due to the availability of OH radicals in the day time. Similarly during night time, the SO<sub>2</sub> concentration increases due to lower PBL heights but the SO<sub>4</sub><sup>2-</sup> concentration decreases due to the non-availability of sufficient OH radicals in the atmosphere.



4.2.1.1.4. December 2009



Figure 4.5: The  $SO_4^{2^2}$  and median of the  $SO_2$  concentrations recorded during each sampling interval for the sampling period in December 2009 over Mt. Abu showing its systematic variation

For the sampling period in December 2009, the SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> variability (figure 4.5) showed least correlation in phase and magnitude. This is explained as due to the major contribution from long range transport to the measured SO<sub>2</sub> over Mt. Abu compared to the local sources as indicated by the large molar S-ratio values. This argument is also discussed in Chapter 3, using the GEOS-Chem model results. When there is relatively higher contribution from long range transport, the SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> variability may not be expected to be correlating in magnitude and phase, due to the different loss mechanisms and mobility patterns for these two species.





Figure 4.6: The  $SO_4^{2^2}$  and median of the  $SO_2$  concentrations recorded during each sampling interval for the sampling period in February 2010 over Mt. Abu showing its systematic variation

During the sampling period in February 2010, the  $SO_2$  and  $SO_4^{2-}$  variations (figure 4.6) were in phase with each other throughout the sampling period. But the magnitude of  $SO_4^{2-}$  variability was found to be much lower than that of  $SO_2$  during the second half of the sampling period, whereas both were matching in magnitude during the initial days of the sampling.

This may either be explained on the basis of more favoring oxidizing conditions in the first half compared to the second half of the sampling period or due to the more contribution from local sources to the measured  $SO_2$  in the second half of the sampling period to result in less aged air mass and hence the lesser conversion.





Mean Time and Date of Sampling

Figure 4.7: The  $SO_4^{2-}$  and median of the  $SO_2$  concentrations recorded during each sampling interval for the sampling period in March 2010 over Mt. Abu showing its systematic variation

During the sampling period in March 2010, the SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> variations (figure 4.7) were more or less in phase with each other with few exceptions. Towards the end of the sampling period, when high intensity SO<sub>2</sub> spikes were present, the SO<sub>4</sub><sup>2-</sup> variation was found to be out of phase with SO<sub>2</sub>, which may be explained on the basis of a long range transport from a strong source region when there is a time lag between the arrival of SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>.

## 4.2.2. The molar S-ratios at Shillong:

At Shillong simultaneous measurements of  $SO_2$  and  $SO_4^{2-}$  were made during the months March 2009 and January 2010. The mean and the median of the molar S-ratio values obtained for March 2009 and January 2010 are given in table 4.2.

	Shillong Site	
Sampling Month	Mean molar S-ratio	Median molar S-ratio
March 2009	0.04	0.03
January 2010	0.32	0.32

Table: 4.2: The mean and median of the molar S-ratio values obtainedexperimentally at Shillong during different sampling periods.

# 4.2.2.1. The SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> variability over Shillong: Major Observations 4.2.2.1.1. March 2009

During the sampling period in March 2009, which saw a transient long range transport of SO<sub>2</sub> from high SO<sub>2</sub> source regions in Russia - as discussed in Chapter 3 - resulting in very high SO<sub>2</sub> concentrations over the sampling site, the molar S-ratio values were very low compared to the molar S-ratios recorded during the sampling period in January 2010. The very low value for the molar S-ratios during March 2009 is explained on the basis of the difference in the mobility as well the loss mechanisms of SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> from the atmosphere. The

low molar S-ratios could also be attributed to the low oxidation efficiency of the atmosphere due to the non-availability of sufficient enough OH radicals – the major oxidizing species in the atmosphere – which were almost completely utilized during the initial days of the transport events itself due to the very high  $SO_2$  concentrations in the ambient atmosphere. The arguments are explained on the basis of the time series  $SO_2$  and  $SO_4^{2-}$  values (shown in figure 4.8) obtained during the sampling period in March 2009.

During March 2009 when a major long range transport event, as discussed in Chapter 3, brought an SO<sub>2</sub> plume with high SO<sub>2</sub> concentrations to the sampling site in Shillong, the SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> variability showed many interesting features. During the days 9<sup>th</sup>, 10<sup>th</sup> and 11<sup>th</sup> of March 2009, the SO<sub>2</sub> variability cannot be explained by the PBL height variations – (against an expectation of higher SO<sub>2</sub> values during night time when the PBL height is low and low SO<sub>2</sub> values during daytime when the PBL height is high) but was found to be randomly varying as if it is governed by the long range transport pattern.

The interesting observation for these days is that the  $SO_2$  and  $SO_4^{2-}$ concentrations are almost 180 degree out of phase with each other. This is well explained on the basis of the difference in the mobility and loss mechanisms of  $SO_2$  (gas) and  $SO_4^{2-}$  (particulate matter) which leads to a delay in the arrival of SO<sub>4</sub><sup>2-</sup> compared to SO<sub>2</sub> at the sampling location in Shillong from the source regions located at very far distances. From 12<sup>th</sup> March 2009 onwards the SO<sub>2</sub> variability is found to be governed by the PBL height variations - ie. High SO<sub>2</sub> values during night time when PBL height is low and low SO<sub>2</sub> values during daytime when PBL height is high. But on  $12^{th}$  also the  $SO_4^{2-}$  concentration was high when SO<sub>2</sub> was low which is again explained by the delayed arrival of  $SO_4^{2-}$ compared to SO<sub>2</sub>. During the days  $13^{th}$  to  $20^{th}$  of March 2009, the SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> are out of phase with each other by almost 180 degree. But since the  $SO_2$ concentration during these days is governed by the PBL height variation as discussed above, the  $SO_4^{2-}$  concentration phase shift is explained by nonavailability of sufficient enough OH radicals in the atmosphere which were eaten up by the high  $SO_2$  concentration during the initial days.



Figure 4.8: The  $SO_4^{2-}$  and median of the  $SO_2$  concentrations recorded during each sampling interval for the sampling period in March 2009 at Shillong showing its systematic variation

Now OH will be produced during daytime via photo chemistry leading to enhanced oxidation of SO<sub>2</sub> during day time compared to night time to give high SO<sub>4</sub><sup>2-</sup> values during day time and low SO<sub>4</sub><sup>2-</sup> values during night time, while the SO<sub>2</sub> concentration is low during daytime due to higher PBL heights and high during night time when the PBL height is low, giving rise to the 180 degree phase shift observed between the SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> variability. During the days 21<sup>st</sup> March to 26<sup>th</sup> March 2009, when the SO<sub>2</sub> concentration values reduced significantly compared to the initial sampling days the SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> variation are in phase with each other indicative of the regain of the oxidation capacity of the atmosphere via sufficient enough concentration of OH radicals in the atmosphere. This above explanation is well justified by figure 4.9 showing the time series molar S-ratio values for the sampling period. The molar S-ratios showed a dip during the days 11<sup>th</sup> and 12<sup>th</sup> of March 2009 which followed a steady increase in the molar S-ratio values which reached its peak value around 20<sup>th</sup> of March 2009.



Mean and Time and Date of Sampling

Figure 4.9: The molar S-ratio values calculated during different sampling intervals for the sampling period in March 2009 at Shillong. The trend seen from the regression line is a dip in the oxidation efficiency during the initial days of the sampling followed by a steady increase

## 4.2.2.1.2. January 2010

For the sampling period in January 2010, which didn't have any major long range contribution, the molar S-ratio values were well within the acceptable limits as will be discussed in the following sections. As against the case with March 2009, a very good correlation is obtained between the SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> values for different sampling periods in January 2010. During the days between  $12^{th}$  and  $19^{th}$  of January 2010, when the SO<sub>2</sub> concentration at the sampling site in


Shillong showed very low diurnal variations, the sulphate concentration as well as the molar S-ratio was found to be pronouncing with strong diurnality pattern.

Mean Time (Hrs) and Date of Sampling

Figure 4.10: The  $SO_4^{2^2}$  and median of the  $SO_2$  concentrations recorded during each sampling interval for the sampling period in January 2010 at Shillong showing its systematic variation

This may be explained on the basis of the back trajectory plots shown in figure 3.1.14 in Chapter 3. It clearly showed that the wind trajectories at altitudes 50m and 500m remain local to create a stagnant atmospheric condition over the sampling site while the trajectory at 3000m altitude carried air parcel from the west Asian region. Such a stagnant air mass ensured an OH dependent diurnal variability patter for  $SO_4^{2-}$  to result in the diurnality observed for this period. From  $20^{\text{th}}$  to  $31^{\text{st}}$  January 2010, when strong diurnality pattern was observed in the SO<sub>2</sub> time series data all three wind trajectories (plotted for altitudes 50m, 500m and 3000m) extended to long distances to cause long range transport of SO<sub>2</sub>. During this period, the molar S-ratio values decreased compared to the previous period - when stagnant air mass was present - which may be explained by the arrival of

sufficient enough  $SO_2$  via transport to compensate the loss of  $SO_2$  due to dry depositions and chemical processes, to keep the  $SO_2$  levels high.

### 4.3. Summary and Conclusions:

The comparative study, aiming at understanding differences in the formation efficiency of  $SO_4^{2-}$  between sites with different environmental conditions, was undertaken during different months over the two study sites Mt. Abu – a remote high altitude site with occasional long range transport of pollutants - and Shilling – a high rainfall site in North East India.

At Mt. Abu simultaneous measurements of  $SO_2$  and  $SO_4^{2^2}$  were performed during the months, September '09, October '09, November '09, December '09, February '10 and March '10. The molar ratio of  $SO_4^{2^2}$  to total sulphur compounds  $(SO_x = SO_2 + SO_4^{2^2})$  termed molar S-ratio defining the formation efficiency of  $SO_4^{2^2}$  (i.e., the amount of  $SO_4^{2^2}$  produced per  $SO_2$  emitted from the emission sources) was calculated for the above sampling periods for our sampling sites Mt. Abu and Shillong.

At Mt. Abu, during the summer months Feb '10 and March '10 the experimentally obtained molar S-ratios were lower compared to the winter months Nov '09 and Dec '09. Intermediate values between these two were recorded during the sampling months Sept '09 and Oct '09, with slightly higher values for the former compared to the latter. The lower S-ratios during the summer months Feb '10 and Mar '10 may be explained by the higher PBL heights compared to the other sampling months and the resulting dilution of SO<sub>2</sub> in the lower layers of the atmosphere to reduce the SO<sub>2</sub> loss from the atmosphere via dry deposition. An increase in the mean free path of the molecules due to higher PBL height - to result in a decrease in the molecular density - also may have resulted in lesser number of collisions between the OH radicals and SO<sub>2</sub> molecules to result in lower conversion efficiencies. Similarly the lower water vapour – a precursor for the OH radical formation in the atmosphere via photo chemistry - content in the atmosphere during the summer months lead to lower concentrations of OH radical to lead to a lowering of the atmospheric oxidation efficiency of SO<sub>2</sub>. Lower relative humilities (RH) during the summer months also reduce the chances of heterogeneous phase oxidation on water droplets, lowering the molar S-ratio values further

The PBL heights during the months November and December are among the lowest of the year leading to a higher loss rate of  $SO_2$  to the ground via the dry deposition – as the  $SO_2$  molecular density near the ground are high under low PBL conditions – and hence a high molar S-ratio. The contribution from long range transport to the  $SO_2$  concentration at the sampling site at Mt. Abu is highest during the months November and December, leading to the presence of aged air masses over the sampling site which results in a higher molar S-ratio. The relative humidity also is on the higher side during these months leading to significant contributions from heterogeneous phase oxidation on water droplets to enhance the molar S-ratio values.

During the months September and October when the molar S-ratios showed intermediate values lying between the summer months (Feb and March here) and the winter months (Nov and Dec here), it is presumable that the molar S-ratios get both positive and negative feed backs from the parameters such as the PBL height, OH radical concentration, Relative Humidity and transport of aged air mass.

A close look at the  $SO_4^{2^2}$  concentration and the median of the  $SO_2$  concentrations recorded in each sampling interval for the sampling period in Sept '09 from which the molar S-ratios were calculated revealed that both  $SO_2$  and  $SO_4^{2^2}$  variations are in phase with each other but with varying magnitudinal difference which is explained as due to a variability in the oxidizing conditions for  $SO_2$  over the sampling site or due to a difference in the source regions for  $SO_2$  from which the long range transport to the sampling site occurred.

In the case of October '09 both  $SO_2$  and  $SO_4^{2-}$  variabilities were in phase during different sampling intervals with the relative difference in the magnitude for  $SO_2$  and  $SO_4^{2-}$  more or less the same throughout the sampling periods indicating the uniformity in the oxidizing conditions prevailing over the sampling site during this month as well as the transport patterns.

During the sampling period in November 09, when a major oil fire erupted at a site located few co-ordinates away from the sampling site at Mt. Abu, the SO<sub>2</sub> and  $SO_4^{2-}$  variability showed a variability which were in phase during the initial few days of the sampling, slowly started moving out of phase and almost 180 degree out of phase in the second half of the sampling period. This is explained as due to the difference in the transit times of  $SO_2$  and  $SO_4^{2-}$  produced during the major oil fire. The other possible explanation is that the fire incident ate away a huge amount of OH radicals – the major oxidizing species in the atmosphere – which resulted in reduction in the oxidation efficiency of the atmosphere at least during the night time.

For the sampling period in December 2009, the  $SO_2$  and  $SO_4^{2-}$  variability showed least correlation in phase and magnitude which is explained as due to the major contribution from long range transport to the measured  $SO_2$  over Mt. Abu compared to the local emissions.

During the sampling period in February 2010, the  $SO_2$  and  $SO_4^{2-}$  variations were in phase with each other throughout the sampling period. During the sampling period in March 2010, the  $SO_2$  and  $SO_4^{2-}$  variations were more or less in phase with each other with few exceptions.

At Shillong the simultaneous measurements of SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> were made during the months March 2009 and January 2010 and molar S-ratios were calculated. During the sampling period in March 2009, which saw a transient long range transport of SO<sub>2</sub> from high SO<sub>2</sub> source regions in Russia resulting in very high SO<sub>2</sub> concentrations over the sampling site, the molar S-ratio values were very low compared to the molar S-ratios recorded during the sampling period in January 2010. This is explained on the basis of the difference in the mobility as well the loss mechanisms of SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> from the atmosphere.

For the sampling period in January 2010, which didn't have any major long range contribution, the molar S-ratio values were well within the acceptable limits. A very good correlation is obtained between the  $SO_2$  and  $SO_4^{2-}$  values for different sampling periods in January 2010.

### Factors influencing the S-ratio: A GEOS-Chem Model based study

### 5.1 Introduction

(Miyakawa et al., 2007), had suggested that seasonal variations in the conversion efficiency of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> could be due to seasonal variations in the boundary layer height and photochemical activity. They proposed that the higher boundary layer height for summer results in reduced loss rate of SO<sub>2</sub> by dry deposition which in turn cause an efficient oxidation of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> before loss onto the surface, with implication to an enhanced S-ratio. Similarly the production rate of OH radical, the major species responsible for SO<sub>2</sub> oxidation in the atmosphere have a dependence on the incoming solar radiation intensity and the water vapour content in the atmosphere, giving way for a season dependent variation in the S-ratio. A seasonal variation in the transport pattern of the polluted air to the sampling site and hence the seasonal variability in the age of the air mass over the sampling site also could contribute to a season dependent variability in the observed molar S-ratio. The seasonal variation in the loss rate of SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> from the atmosphere through the dry deposition process also can influence the S-ratio.

Via extensive use of the GEOS-Chem model, the relative contribution of each of the above parameters to the molar S-ratio is systematically studied in this chapter. The diurnal variability in the molar S-ratios generated using the model also is discussed. The molar S-ratio variation as function of altitude during different seasons of the year also is studied in this chapter and its possible reasons are explored.

### 5.2. The seasonal variation in S-ratio from GEOS-Chem model

Figure 5.1 shows the molar S-ratios calculated using GEOS-Chem for different months of the year 2009. For this the time series  $SO_2$  and  $SO_4^{2-}$  values for the nearest co-ordinates (26<sup>0</sup> N, 75<sup>0</sup> E) to the Mt. Abu site available with the

model, was generated for each month and the molar S-ratios were calculated using the formula mentioned in Chapter 2. Similar to the experimental observations in Chapter 4, the molar S-ratios calculated from the model also showed a seasonal dependence with the highest values recorded during July and August, and the lowest recorded in the month of April. The trend observed is a steady increase in S-ratio values from April till July; remain steady in August, followed by a decrease till November. The S-ratio values again switch to the accenting mode during December and January followed by a steady descent to reach the lowest value of the year in April.





It is presumable that this systematic variation in S-ratio as function of season is dictated by the season dependent changes in the various atmospheric parameters directly or indirectly influencing the SO<sub>2</sub> oxidation process in the atmosphere. Some of these factors are: a) the OH radical concentration in the atmosphere, b) the Planetary Boundary Layer (PBL) height variation, (c) the Relative Humidity (RH), (d) the dust load in the atmosphere, (e) the dry

deposition rate of  $SO_2$  and  $SO_4^{2-}$ , (f) the variation in the transport pattern etc. All these parameters can provide feedback to the  $SO_2$  oxidation process either positively or negatively, to give the seasonal pattern shown in the Figure 5.1. The relative contribution of the above parameters to the S-ratio variation is discussed in the following sections. In addition to the seasonal variation, the S-ratio calculated from the model was found to vary diurnally also as will be discussed in the next sections.

### 5.3 Major parameters controlling the S-ratio: The model results

### 5.3.1 OH radical concentration versus PBL height variations:

The OH radical concentration and PBL height for the first day of each month of the year 2009 was generated using GEOS-Chem and the plots are shown in figures 5.2 and 5.3.







35°N

30°N

25°N

20°N

15°N

10°N

65%

766376







Figure 5.2: OH radical concentration (molecules/cm<sup>3</sup>) recorded on the 1<sup>st</sup> day of each month of the year 2009, generated using GEOS-Chem for the Indian region, showing its seasonal variability

Both the OH radical concentration as well as the PBL height was found to vary as function of season. In the case of OH radical (figure 5.2), the concentrations recorded high values during the months May to September, with the highest value of the year recorded in July. Similarly for different months the PBL heights were found to be systematically varying (figure 5.3), recording high values during the months February to June.

Since both OH radical as well as PBL height can contribute to the  $SO_2$  seasonal variability, a systematic study is made on the dependence of  $SO_2$  on the OH radical concentration as well as the PBL height for all the months of the year 2009 using GEOS-Chem and is discussed as follows.

The Figure 5.4 shows the variation in the Molar S-ratio as function of OH radical concentration and PBL height plotted for different months of the year 2009 for the co-ordinates  $(26^{\circ} \text{ N}, 75^{\circ} \text{ E})$ . For this the time series OH radical concentrations and PBL heights were generated for the co-ordinates  $(26^{\circ} \text{ N}, 75^{\circ} \text{ E})$  using the GEOS-Chem model. The time series S-ratio values calculated using the time series SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> values were then plotted against the corresponding OH and PBL values for different months of the year 2009.



GEOS5 47L PBL-M 090301 at 08:00 GMT L=1 (0.3 km GEOS5 47L PBL-M 090401 at 08:00 GMT L=1 (0.3 km











Figure 5.3. PBL height (meters) recorded on the 1<sup>st</sup> day of each month of the year 2009, generated using GEOS-Chem for the Indian region, showing its seasonal variability

For the month January, when the PBL height is below 500 m, the molar S-ratio remained high irrespective of the OH radical concentration. Similarly above a PBL height of 1000 m, the molar S-ratio remained high for all OH radical concentrations lying between  $1e^{+6}$  and  $6e^{+6}$ . The plot showed random peaks and troughs also, suggesting the presence of other atmospheric parameters capable of controlling the oxidation efficiency of SO<sub>2</sub> in the atmosphere, under the climatical conditions prevailing in this month.

In the case of February, the random peaks observed in the previous month almost vanished suggesting the prominent roles played by the PBL height and OH radical concentration in controlling the molar S-ratio, under the climatical conditions prevailing in this month. The molar S-ratio remained high when the PBL height is below ~300m.







GEOS - Jul '09

0.0 0.2 0.4 0.6 0.8 1.0

1.0

Molar 0.2

0.0

1.2e+7

OH Conc (Number density)

4.0e+6

2.0e+6





500

1000 P81-Height(m)

2000



Figure 5.4: The variation in the molar S-ratio as function of OH radical concentration (molecules/cm<sup>3</sup>) and PBL height (m) plotted for different months of the year 2009 for the co-ordinates ( $26^{\circ}N$ ,  $75^{\circ}E$ )

The relatively lower S-ratio for this month may be explained by the fact that, it is mostly the local sources which contribute to the atmospheric  $SO_2$  for this month – as seen in Chapter 3 that percent reduction in  $SO_2$  concentration in the absence of the transport is low for the month of February. Once the sources are local, and the long range transport contribution is minimum, the air parcel is less aged and lead to lesser amount of  $SO_2$  conversion to  $SO_4^{2-}$  and hence the lower S-ratio. This probably gives an idea that by looking at the S-ratio, one can talk about the age of the air parcel at this site and hence about the long range transport events occurring to this site.

The S-ratio for the month March also is on the lower side, which may be attributed to the predominance of local sources in controlling the SO<sub>2</sub> concentration compared to the long range transport leading to the non-availability of aged air masses and hence the observed low S-ratio. The S-ratio was on the higher side when the PBL height was below ~ 700 m for all OH concentrations of the month (lying between  $1e^{+6}$  and  $8e^{+6}$ ). The oxidation efficiency was observed to increase with OH concentration values between  $6e^{+6}$  and  $7e^{+6}$ , which followed a decrease in efficiency with OH concentration values above  $7e^{+6}$ , suggesting the above range to be the optimum one under the climatical conditions prevailing in the month of March for maximum SO<sub>2</sub> conversion to SO<sub>4</sub><sup>2-</sup>. The molar S-ratio switched to the higher side for PBL heights above 2500 m, with some dependence

on the OH concentration. Also some random peaks for the molar S-ratio was observed in this month which may be attributed to the random transport of the aged air mass to the sampling site.

In the month of April, the PBL height maximum reached ~4000m, but the OH radical concentration maximum remained the same as the one for March and the molar S-ratio recorded the lowest value of the year. This may be explained as follows. The higher PBL height leads to a dilution of the available OH radical density, as the OH radical concentration didn't increase in the same rate as that of the PBL height increase when proceeding from March to April, which may be due to the non-favourable atmospheric parameters for the formation of OH radicals under the climatic conditions prevailing in this month. The lower amount of OH radical density lead to a lower oxidation efficiency and hence the observed low molar S-ratio. As shown in chapter 3, in the month of April the SO<sub>2</sub> contribution from long range transport to the sampling site at Mt. Abu is lowest leading to the negligible amount of aged air mass and hence the observed lowest molar S-ratio, in addition to the factors discussed previously. The molar S-ratio remained high for all PBL heights below ~500 m, independent of the OH radical concentration. Similarly, for OH radical concentration between  $1e^{+6}$  and  $3e^{+6}$ , the molar S-ratio remained high till a PBL height of ~ 3000 m - and was found to be shifting towards the higher OH values with PBL height increase, beyond which the value started decaying.

In the month of May, when the molar S-ratio switched to the ascending mode after the lowest value of the year recorded in April, the PBL heights were mostly below ~ 3500 m and the OH radical concentration maximum reaching ~  $10e^{+6}$  while the minimum value maintaining above  $1e^{+6}$ , the S-ratio remained high for PBL values below ~1000 m for all OH radical concentrations below  $8e^{+6}$ . For PBL heights below ~1000 m, the S-ratio was found to be decreasing for OH radical concentrations above ~  $8e^{+6}$ . For higher PBL heights, the molar S-ratio was found to be increasing with increasing OH radical concentration.

In the month of June, above an OH concentration of ~  $1e^{+7}$ , the molar Sratio is high for all the PBL heights of the month. For PBL heights below ~1000m, the molar S-ratio is high for OH concentrations between  $2e^{+6}$  and  $1e^{+7}$ .

143

Many random peaks are observed for this month, which may be attributed to the random transport of aged air masses as well as the presence of heterogeneous phase chemistry on cloud droplets due to higher RH values present occasionally, as will be discussed in the next sections.

In the month of July, when the PBL height recorded a maximum of only ~2000m, and OH radical concentration is among the highest of the year, the molar S-ratio remained high for most of the combinations of OH radical concentration and PBL heights. Possibility of heterogeneous phase oxidation on cloud droplets is another reason for the higher molar S-ratios for this month. A combination of lower PBL heights, higher OH radical concentration along with possible heterogeneous phase oxidation on cloud droplets due to high relative humidity (RH) makes the SO<sub>2</sub> oxidation efficiency high for this month.

In the month of August, when the molar S-ratio is among the highest values of the year, the PBL height recorded a maximum of only  $\sim$ 1400 m – the lowest value of the year, and the OH radical concentration remained high. The combination of low PBL height and high OH radical concentration along with the possibility of heterogeneous phase oxidation due to high RH, keep the molar S-ratio the highest of the year.

In the month of September, when the PBL heights increases above it value for August and the OH radical concentrations start decreasing, the molar S-ratio also started decreasing. Random peaks were observed for this month, which may be attributed to the random arrival of aged air mass or the random variations in the RH values.

In the month of October which also saw a decrease in the molar S-ratio values, the PBL height started increasing further and the OH radical concentration decreased below its value for the previous month. Below ~ 500 m PBL height, the molar S-ratio remained high for all OH radical concentrations. Few random peaks also were noted in this month.

In the month of November the PBL height maximum and OH radical concentration remained the same as that for October. But for this month, there were very few cases when the PBL height minimum went below 500 m, reducing the oxidation efficiency of  $SO_2$  and recorded a dip in the mean molar S-ratio.

144

In the month of December, when the mean molar S-ratio again switched to the ascending phase, the PBL height maxima decreased below its value for November. Similarly, there were many cases when the PBL height remained below 500m as against the previous month, leading to more conversion efficiency. Another reason for the higher S-ratio for this month is attributed to the dominant role of long range transport in controlling the SO<sub>2</sub> concentration over the sampling site at Mt. Abu. As is discussed in Chapter 3, Mt. Abu sees a large contribution coming from long range transport in the month of December and hence leads to the presence of aged air mass over the sampling site leading to the enhanced Sratio.

5.3.2. OH radical concentration versus RH: The homogeneous versus heterogeneous phase chemistry

The relative humidity variation as function of season generated using GEOS-Chem for the Indian region is shown in figure 5.5. The relative humidity (RH) show high values during the months July, Aug, Sept and October. During the times the RH is high the heterogeneous phase oxidation on water droplets is expected to play crucial roles in controlling the conversion efficiency of SO<sub>2</sub> in the atmosphere. To validate these, a systematic study on the dependence of molar S-ratio on the RH and OH radical concentration is made and is discussed below. In order to understand the role of heterogeneous phase oxidation, plots were made (figure 5.6) - using the data generated from the GEOS-Chem model - with molar













S-ratio as functions of OH radical concentration and RH for different months of the year 2009.In January 2009, the molar S-ratio was found to be increasing along with increase in RH as well as OH radical concentration. For this month, the RH is mostly below 50%, and hence the heterogeneous phase chemistry is not expected to play significant roles.

In February, when the RH maximum is only 50%, the conversion efficiency was found to be high for low OH radical concentrations (with few exceptions). As in the case of January, the heterogeneous phase chemistry is not expected to play crucial roles, in view of the low RH for this month. For the months, March and April, the molar S-ratios are possibly controlled by homogeneous as well as heterogeneous phase chemistry along with high PBL height values and random transport as evidence by the random peaks observed for these months.





GEOS - May '09









Figure 5.6: The variation in the molar S-ratio as functions of OH radical concentration (molecules/cm<sup>3</sup>) and RH (%) plotted for different months of the year 2009 for the co-ordinates  $(26^{\circ}N, 75^{\circ}E)$ 

In the month of May – the month from which the acceding phase for the mean molar S-ratios starts - above an OH concentration of  $3e^{+6}$ , the molar S-ratio values are found to be high for all RH values of the month.

In the month of June, when the RH values switch to the ascending phase, molar S-ratio values were on the higher side. The OH radical – produced photochemically in the atmosphere - concentration maxima also increased to ~  $1.4e^{+7}$ , which is attributed to the higher water vapour content as well as high insolation for this month. In the month of July, when the RH values lie between 40% and 95%, the molar S-ratio values were on the higher side. For RH values above ~45%, the molar S-ratio values were higher compared to RH values below ~45%.

In the month of August, which recorded the highest mean molar S-ratio of the year, the heterogeneous phase oxidation on cloud droplets is the major player in the SO<sub>2</sub> oxidation in the atmosphere compared to the homogeneous phase chemistry. For this month, the RH values lie between ~65% and 98% and the molar S-ratio was found to be independent of the OH radical concentration above an OH concentration value of  $2e^{+6}$ . Another interesting observation for this month is that, above a RH value of ~85%, the molar S-ratio values switch to the lower side possibly has association with the wet deposition of SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> at this high RH values.

In the month of September, when the mean molar S-ratio values switch to the descending phase, the RH as well as the OH radical concentration is lower than that for the previous month. The contribution from heterogeneous phase chemistry starts to decrease and hence the molar S-ratio decreases below its value for the previous month. In the month of October when the mean molar S-ratio further decreases, the OH radical concentration as well as the RH values saw a further decrease in values compared to September. The molar S-ratio values switch to higher values beyond an OH radical concentration of ~  $5e^{+6}$ .

In the months, November and December, the molar S-ratio dependence is found to be similar to those of January, discussed above. A dependence of molar S-ratio on both RH values as well as OH concentration is observed as evidenced by the high molar S-ratio values noted diagonally in the graphs.

#### 5.3.3 Effect of Atmospheric Dust load on the molar S-ratio over Mt. Abu

To understand the possible effect of heterogeneous phase oxidation on dust surfaces on the Molar S-ratio over the semi-arid site Mt. Abu - characterized by high abundances of mineral dust - GEOS-Chem model runs were performed with Dust emissions turned OFF. The S-ratios from this model run - with all parameters except dust emission turned ON - was calculated and the percent difference in molar S-ratio in the absence of dust emission is calculated as follows.

#### Percent Difference in molar S-ratio in the absence of Dust Emission

#### = (WithOutDustEmission – FullInput)\*100/FullInput

where:

# WithOutDustEmission $\rightarrow$ Molar S-ratio calculated from the run with dust emission OFF

## FullInput $\rightarrow$ Molar S-ratio calculated from the run with all parameters turned ON

The figure 5.7 shows the seasonal variation in the 'percent difference in molar S-ratio values' in the absence of dust emission. The major observation is that in the absence of dust emission, the molar S-ratio and hence the  $SO_2$  conversion to  $SO_4^{2-}$  is decreased below its value for Full Input run. This underlines the fact that heterogeneous phase oxidation on dust surfaces leads to conversion of more  $SO_2$  to  $SO_4^{2-}$  and hence to global cooling. The percent difference in molar S-ratio, in the absence of dust emission, is found to be maximum during the moths Feb, Mar, April and May, with maximum difference recorded in the month of May, which is the month with the highest dust loading in the atmosphere over this semiarid site. The model calculated a maximum of 4.7% (median value) enhancement in the  $SO_2$  oxidation efficiency due to heterogeneous oxidation on dust, under the highest dust loading conditions in May over the sampling site at Mt. Abu.



Figure 5.7: The Percentage difference in molar S-ratio values in the absence of dust emission for the co-ordinates  $(26^{\circ} N, 75^{\circ} E)$ .

5.3.4. Effect of Transport on the molar S-ratio over Mt. Abu

In order to understand the effect of transport on the S-ratio over Mt. Abu, GEOS-Chem model runs were performed with Transport Turned OFF in the model. Now only the SO<sub>2</sub> emitted within the cell of  $4^0 \times 5^0$  and the chemistry and losses only controls the S-ratio. Now the percentage difference in the molar S-ratio between the two runs (ie. One with Full Input and the other with all parameters in the previous one except for the transport ON) is calculated as

### Percent Difference in molar S-ratio in the absence of Transport

= (WithOutTransport – FullInput)\*100/FullInput

where:

WithOutTransport → Molar S-ratio calculated from the run with Transport mechanism OFF

## FullInput $\rightarrow$ Molar S-ratio calculated from the run with all parameters turned ON

The results are shown in figure 5.8. The percent difference in molar S-ratio showed a seasonal dependence with values oscillating in the positive and negative direction as function of season. During the months Jan, Feb, Mar, April and May, the molar S-ratio enhanced in the absence of transport mechanism above its value for full input with the highest value recorded in the month of April. Lower values were recorded during the months Jun, July, Aug, Sept and Oct with the lowest value of the year recorded in July. The ascending phase starts from the month of November.



# Figure 5.8: The Percentage difference in molar S-ratio values in the absence of Transport for the co-ordinates $(26^{0} N, 75^{0} E)$ .

5.3.5 Effect of Dry deposition on the molar S-ratio over Mt. Abu

To understand the possible effect of a seasonal variation in the dry deposition of  $SO_2$  and  $SO_4^{2-}$  on the molar S-ratio over the semi-arid site of Mt. Abu characterized by high abundances of mineral dust, GEOS-Chem model runs were performed with dry deposition turned OFF. The S-ratios for the model runs

with all parameters turned ON except dry deposition was calculated and the percent difference in molar S-ratio in the absence of dry deposition is calculated as follows.

### Percent Difference in molar S-ratio in the absence of dry deposition = (WithOutDryDeposition – FullInput)\*100/FullInput

where:

# WithOutDryDeposition $\rightarrow$ Molar S-ratio calculated from the run with dry deposition OFF

## FullInput $\rightarrow$ Molar S-ratio calculated from the run with all parameters turned ON

The figure 5.9 shows the percent difference in molar S-ratio values in the absence of dry deposition for different months of the year 2009. The major observation is that in the absence of dry deposition, the molar S-ratio decreased below its value for Full Input run. This is explained by the known fact that  $SO_2$  is more prone for the physical removal via the dry deposition process compared to  $SO_4^{2^-}$ . The percent difference in molar S-ratio in the absence of dry deposition is found to be maximum during the month of August followed by July, underlining the fact that the dry deposition rate is enhanced when clouds are present – as is the case with these high rainfall months.

The model calculated a maximum of ~ 66.3% (median value) enhancement in the molar S-ratio when dry deposition is present compared to the case in which the dry deposition is absent (in the month of August), over the coordinates ( $26^0$  N,  $75^0$  E). The effect of switching OFF the dry deposition on the molar S-ratio is found to be a minimum during the months March, April and May with the lowest deviation recorded in the month of May. These may be explained by the fact that during these months the boundary layer heights are very high leading to lesser amount of SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> in the lower layer of the atmosphere, to reduce the loss due to the dry deposition process.



Figure 5.9: The Percentage difference in molar S-ratio values in the absence of dry deposition for the co-ordinates  $(26^{0} N, 75^{0} E)$ .

### 5.4 Diurnal variation in molar S-ratio

The diurnal variation observed for the molar S-ratio (Figure 5.10) was found to be different in magnitude for different months of the year even though the general trend of an increase in the molar S-ratio values during sun lit hours with the peak obtained for the highest insolation time – remain the same for all the months. This general trend is explained by the well accepted process of  $SO_2$ oxidation by OH radical produced photo-chemically in the atmosphere. The OH radical is present only when insolation is sufficiently high, leading to an insolation dependent variation in the  $SO_2$  oxidation rate in the atmosphere.

During the month of January, the S-ratio showed a minimum at 0600 hrs followed by sudden rise at 0800 hrs which a steady increase to reach the maximum at 1400 hrs followed by a steady decrease. Another feature for this month is that the spread in S-ratio values was on the higher side, probably due to disturbances in the transport patterns of  $SO_2$  and  $SO_4^{2-}$  as well as the non-systematic variations in the atmospheric parameters controlling the S-ratio.

During February, the trend remain similar to that of January, but now the molar S-ratio remain high till 1600 hrs compared to the 1400 hrs in January. This may be explained as due to an increase in the insolation levels as one proceed from January to February casing the OH radical – a major oxidising species for SO<sub>2</sub>, and produced photo-chemically in the atmosphere - concentration in the atmosphere to remain high till 1600 hrs. The spread in molar S-ratio values for this month is on the lower side, probably has association with factors favouring a uniform conversion rate such as a relatively lower contribution from random long range transport as discussed in Chapter 3.

Similarly, the trend for March is more or less similar to February except that the spread in molar S-ratio values are slightly above that of the previous month. The step increase in S-ratio value between 0600 hrs and 0800 hrs also is slightly larger compared to the previous month which may be explained with the availability of more intense insolation even during the early morning hours.

For the month April - projected as the month with lowest molar S-ratio in the GEOS-Chem model generated graphs - the molar S-ratio increase between 0600 hrs and 0800 hrs is more rapid compared to March. The molar S-ratio continue to increase till 1600 hrs rather than remaining steady at the value at 1400 hrs, again probably has to do with the availability of intense insolation even during afternoon hours. The spread in molar S-ratio for this month is on the lower side.







Figure 5.10: The diurnal variation observed for the molar S-ratio for different months of the year 2009, using GEOS-Chem

During May – from which month the mean molar S-ratio switch to the ascending phase - the molar S-ratio values recorded during early morning hours is higher compared to the previous months, resulting in a less rapid step increase between 0600 hrs and 0800 hrs. The spread in molar S-ratio values is on the lower side, probably indicating factors favouring a uniform conversion of SO<sub>2</sub>.

During June, the general trend remain similar to those of May except that the spread in molar S-ratio values is higher, which may be explained as due to the transient variation in the various atmospheric parameters controlling the oxidation efficiency of  $SO_2$  leading to a non-uniform conversion rate and hence the observed spread.

During July, when the rain starts and the relative humidity (RH) increases, enhancing the probability for heterogeneous phase oxidation on water droplets, the diurnal pattern show a slightly different trend with the molar S-ratio peak attained at 1200 hrs followed by a decrease in S-ratio values. The ascending mode for molar S-ratio starts at 0600 hrs, ~2 hrs early compared to the previous month. A sudden drop in molar S-ratio value between 1600 hrs and 1800 hrs is another noted feature for this month compared to the previous months.

In August, when the RH for the region and hence the possibility for heterogeneous phase chemistry is highest, the diurnal pattern is similar to the one obtained for June, except for a larger spread in molar S-ratio values. As discussed in the previous session, it is in the month of August, the highest molar S-ratio for this region recorded in the GEOS-Chem generated molar S-ratio values, and would probably has association with an enhanced contribution from heterogeneous phase oxidation because of the high RH values.

In September, the spread in molar S-ratio values were small between 1800 hrs and 2400 hrs, compared to the other periods of the day, and may have association with a diurnal variation in the transport pattern, when the source region for the  $SO_2$  reaching the sampling site are different, leading to difference in the  $SO_2$  spikes and hence the spread.

During October, the diurnal variability decreased compared to the previous month. The ascending mode of molar S-ratio extends to 1600 hrs. During the months November and December, the diurnality increases above its values for October, with a dip at 0600 hrs and a peak at 1400-1600 hrs. The molar S-ratios showed larger spread in their values for December compared to November.

#### 5.5 Variation in molar S-ratio as function of altitude above ground level

To study the altitudinal dependence of  $SO_2$  oxidation efficiency, molar Sratios at different altitudes were calculated from the GEOS- Chem model and graphs were plotted. The calculations were performed for the months May, July, and December 2009 representing three different seasons and so having different mean Planetary Boundary Layer (PBL) heights as well as climatic conditions. In all three cases altitude variation in S-ratios were noted but with different features.

For the month May 2009, which represents a summer month, the molar Sratios (Figure 5.11) increased above its value for ground level (below 0. 3km) till an altitude 0.9 km above the surface. The molar S-ratio then remained steady till an altitude of 3.3 km. A second ascending phase in molar S-ratio values started from 3.6 km. The spread in molar S-ratio was highest at the ground level which decreased in magnitude till an altitude of 0.9 km and from there the spread remained more or less steady till 4.2 km. This spread in molar S-ratio values for the lower altitudes may be attributed to the air turbulence and the associated





Figure 5.11: Variation in molar S-ratio as function of altitude above ground level for the summer month, May 2009 for the co-ordinates  $(26^{\circ}N, 75^{\circ}E)$ .

The altitude variation in the molar S-ratio for the month of July (Figure 5.12), which is a high rainfall month, differs from that for the month of May. In this month, the molar S-ratios increased in magnitude till it reached an altitude of 3 km where it remained more or less steady till 3.9 km followed by a slight increase. The sudden increase in the mean molar S-ration value between the altitudes 0.3 km and 0.6 km showed similarity to the one persisted in the May and may be explained as due to the air turbulence and the associated variations in the transport and loss mechanisms for SO<sub>2</sub>. The spread in S-ratio values remained high. For the month of December, which is a winter month with a low mean PBL height, the altitude variation in the molar S-ratio showed features (Figure 5.13) different than the other two months discussed above. After a slight increase in the molar S-ratio values from 0.3 km to 0.6 km AGL, the molar S-ratio remained



Figure 5.12: Variation in molar S-ratio as function of altitude above ground level for the month, July 2009 for the co-ordinates  $(26^{\circ}N, 75^{\circ}E)$ .



Figure 5.13: Variation in molar S-ratio as function of altitude above ground level for the winter month, December 2009 for the co-ordinates  $(26^{\circ}N, 75^{\circ}E)$ 

steady till 2.7 km AGL which followed a steep increase in the molar S-ratio values.

#### 5.5 Summary and Conclusion

Via extensive use of the GEOS-Chem model, the relative contribution of various parameters such as OH radical concentration, Relative humidity, Planetary Boundary Layer height, dust load in the atmosphere, the dry deposition process, long range transport etc to the molar S-ratio is systematically studied.

The molar S-ratios calculated using GEOS-Chem for different months of the year 2009 for the co-ordinates ( $26^0$  N,  $75^0$  E) showed a seasonal dependence with the highest values recorded during July and August, and the lowest recorded in the month of April.

Both the OH radical concentration as well as the PBL height was found to vary as function of season. In the case of OH radical, the concentrations recorded high values during the months May to September, with the highest value of the year recorded in July. Similarly for different months the PBL heights were found to be systematically varying, recording high values during the months February to June.

Since both OH radical as well as PBL height can contribute to the  $SO_2$  seasonal variability, a systematic study is made on the dependence of  $SO_2$  on the OH radical concentration as well as the PBL height for all the months of the year 2009 using GEOS-Chem which showed the varying contribution of PBL height and OH radical concentration in controlling the molar S-ratio during different months.

Similarly, the relative humidity variation as function of season generated using GEOS-Chem for the Indian region showed high values during the months July, Aug, Sept and October. During the times the RH is high the heterogeneous phase oxidation on water droplets is found to play crucial roles in controlling the conversion efficiency of  $SO_2$  in the atmosphere.

In the absence of dust emission, the molar S-ratio and hence the  $SO_2$  conversion to  $SO_4^{2-}$  is decreased below its value for the Full Input run. The

162

percent difference in the molar S-ratio when transport is turned OFF showed a seasonal dependence with values oscillating in the positive and negative direction as function of season.

Similarly it was found that in the absence of dry deposition, the molar S-ratio decreased below its value for Full Input run. This is explained by the known fact that  $SO_2$  is more prone for the physical removal via the dry deposition process compared to  $SO_4^{2^2}$ .

### Chapter 6

### Synthesis and scope of future research

### 6.1. Synthesis:

Sulphur gases including sulphur dioxide (SO<sub>2</sub>), dimethyl sulphide, hydrogen sulphide, carbon disulfide and carbonyl sulphide plays multi-roles in the chemistry of global troposphere and in the biogeochemical sulphur cycle. Out of these major sulphur gases SO<sub>2</sub> has special significance for it is an important air pollutant. It plays roles in controlling the oxidizing power of the atmosphere and air quality, cause acid rain and modify atmospheric radiative forcing pattern via gas-phase chemistry and particle formation. There has been a regional shift in the emissions of SO<sub>2</sub> from the US and Europe to south-east Asia - characterized by a rapid increase in energy consumption, fast growing population and increased economic activities - leading to significant shift in the atmospheric radiative forcing patterns in these regions. In this context it is very relevant to make SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> measurements over sites with varying environmental conditions. A comparative study between semi arid high-altitude sites having free tropospheric characteristics with semi-arid sites lying at relatively lower altitudes can help understand the transport pattern of SO<sub>2</sub> in the free troposphere.

Similarly  $SO_2$  and  $SO_4^{2-}$  measurements over sites with a high rainfall and strategically located near the known high polluted regions in Asia, can improve upon the current understanding on the roles of long range transport in controlling pollutant characteristics over such relatively cleaner sites. It is known that the sulphate aerosols, the oxidation product of sulphur gases, influences global as well as regional climate via acidification and perturbation of atmospheric radiative forcing through new particle formation and cloud microphysics with implication to introduce large uncertainties in the assessments of climate change. Aerosol sulphate is produced in the atmosphere predominantly by the oxidation of its
precursor species  $SO_2$  via both heterogeneous and homogeneous pathways and the oxidation rate increases with relative humidity.

A factor, S-ratio, defined the ratio of particulate S (as  $SO_4^{2-}$ ) to total S (as  $SO_2$  and  $SO_4^{2-}$ ) can be used as a parameter to track the average formation efficiency of  $SO_4^{2-}$  (i.e., the amount of  $SO_4^{2-}$  produced per  $SO_2$  emitted from the emission sources) in the atmosphere for different seasons and environmental conditions. The ratio is an indicator of air mass age, chemical conversion efficiency and "en route" deposition and in general the S-ratio can be used as measure of the formation efficiency of  $SO_4^{2-}$ . Spatio-temporal changes in various atmospheric parameters directly influencing the chemical conversion efficiency of  $SO_2$  to  $SO_4^{2-}$  as well as differences in the loss rate of  $SO_2$  and  $SO_4^{2-}$  from the atmospheric parameters can influence the atmospheric oxidation efficiency of  $SO_2$  and hence the S-ratio, such as OH radical concentration, atmospheric dust content, planetary boundary layer height variation, relative humidity, season dependent variation in the long range transport of pollutants to the sampling site, the variation in the dry deposition rate etc.

The present study have the specific objectives of providing quantitative information on the surface level concentrations of gaseous SO<sub>2</sub> from three sites in India characterised by distinctly different emission sources, wind regimes, atmospheric transport and abundance of mineral dust. The second major objective of the work is to assess the temporal and spatial variability in the sulphur conversion ratio (S-ratio) - the molar ratio of SO<sub>4</sub><sup>2-</sup> to total sulphur compounds (SO<sub>x</sub> = SO<sub>2</sub> + SO<sub>4</sub><sup>2-</sup>), which is a measure of the atmospheric oxidation efficiency of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup>. The experimentally obtained results are compared with a famous chemical transport model, GEOS-Chem, generated results.

Also the model is used to understand the relative contribution of various parameters controlling the S-ratio such as the OH radical concentration, relative humidity, Planetary Boundary Layer height, dry deposition rate, atmospheric dust content, long range transport etc., which was not feasible with the available experimental setup.

The ambient SO<sub>2</sub> concentrations at Shillong (25.67°N, 91.91°E, 1064 m ASL), a high rain fall site located in North East India, measured during March 2009 and January 2010 showed significant differences in magnitude, with concentrations going to a maximum of 262.3 ppbv during the former sampling period—which decayed down gradually towards the end the sampling period against the maximum value recorded during the latter period of 29.7 ppbv. This elevated SO<sub>2</sub> concentrations during March 2009 is explained as due to a long range transport associated with the cold air outbreak preceding one of the dust storm events reported in China. This argument of long range transport for the observed high SO<sub>2</sub> values during March 2009 is formulated on the basis of the back trajectory analysis performed using HYSPLIT for the sampling period—the plots clearly showed a drastic change in wind trajectories between 8th and 15th of March 2009 wherein the winds travelled over some of the highly polluted regions such as the Perm region of Russia-and on the basis of the results from simulations performed using the global 3-D model of tropospheric chemistry, GEOS-Chem (v8-03-01)—it clearly showed the tropospheric SO<sub>2</sub> over Perm region peaking during November, December, January, February and March every year, possibly due to central heating. The observation of long range transport of SO<sub>2</sub> from the highly industrialized areas of Perm in Russia to North-East India during the dust storm event in March 2009 is projected to have important implications to its share in the Asian pollutant outflow to the Pacific during spring, every year. Separate runs of the model revealed that the regions in and around Russia have high concentrations of other atmospheric pollutants such as NOx, Peroxyacetyl Nitrate, Lumped Peroxypropionyl Nitrate, HNO<sub>3</sub>, HNO<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>2</sub>H<sub>6</sub>, SO<sub>4</sub>, NH<sub>4</sub>, Inorganic Sulphur Nitrates and Lumped Alkyl Nitrate. The model runs also showed that some of the other atmospheric pollutants such as N<sub>2</sub>O<sub>5</sub>, NH<sub>3</sub>, hydrophilic black carbon, hydrophilic organic carbon, hydrophobic black carbon and hydrophobic organic carbon are present only in negligible levels in the Perm region compared to the other polluted regions in North-East Asia and so will not contribute significantly to the Asian pollutant outflow.

The comparison of the time series  $SO_2$  profile obtained for the nearest coordinates (26°N, 90°E) from the GEOS-Chem model with the experimental data,

for the month of March 2009, revealed that the model was not able to pick up the magnitude of this transport whereas there is a good correlation between the two for January 2010. Similarly ambient SO<sub>2</sub> concentrations were measured from the semi arid high altitude site, Mt. Abu, during the months Feb '09, Sept '09, Oct '09, Nov '09, Dec '09, Feb '10 and Mar '10 with the aim to understand the seasonal variability in SO<sub>2</sub> levels over this semi-arid high altitude site. The GEOS-Chem Chemical Transport Model is used to generate the SO<sub>2</sub> profile for the Indian region for the sampling months which helped identifying the major  $SO_2$ source regions. Now by analysing the back trajectories generated using HYSPLIT for the sampling periods – performed at different altitudes to investigate the source and the transport pathways of pollutants before they reach the measurement locations - and correlating them with the GEOS-Chem generated SO<sub>2</sub> plots showing the SO<sub>2</sub> source regions, the observed peaks in the measured SO<sub>2</sub> spectrum is explained. The GEOS-Chem plots for SO<sub>2</sub> over India showed the region around co-ordinates  $30^{\circ}$  N and  $75^{\circ}$  E with very high concentrations of SO<sub>2</sub> throughout the year offering the possibility of long range transport of SO<sub>2</sub> including the free tropospheric transport - to the sampling site at Mt. Abu located only a few co-ordinates away.

During February '09 when the wind back trajectories extended to regions located around co-ordinates  $30^{0}$  N and  $75^{0}$  E lying North and North-East of the sampling site, the time series profile has many spikes with a mean concentration of 4.3 ppbv and a standard deviation of 0.792 ppbv, emphasizing the prominent role of long range transport in controlling the ambient SO<sub>2</sub> levels over this high altitude remote site under the climatic conditions prevailing here in month of February. The SO<sub>2</sub> profile showed some sort of a diurnal variation pattern with the minimum concentration values reported between 0700 hrs and 1000 hrs IST which is explained as due to a sudden rise in the boundary layer height and a consequent dilution of the SO<sub>2</sub> concentration at the ground level as well as the rapid increase in the OH radical concentration - which increases the SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> conversion rate.

During Sept - Oct '09, when the winds originated mostly from Arabian Sea the  $SO_2$  concentration measured at Mt. Abu showed a near constant value

with very few spikes – which very well correlated with a change in trajectory pattern when long range transport from high  $SO_2$  source region around the coordinates,  $30^0$  N and  $75^0$  occurred. The mean and standard deviation of the concentration values obtained during the sampling period are 4.3 ppbv and 0.208 ppbv respectively. The absence of diurnal variability during this period is explained as due to the very high OH radical concentration present during these months for a higher water vapour content and insolation rate.

During the sampling period in November 2009, the  $SO_2$  time series data had a mean and standard deviation recorded of 3.4 ppbv and 1.25 ppbv respectively. The back trajectories showed pollutant transport from the high SO<sub>2</sub> region located around  $30^{0}$  N and  $75^{0}$  E as well as low SO<sub>2</sub> source regions in the GEOS-Chem generated maps for the Indian region. Because of the wind pattern specific for this month, only short duration random air parcels from the high SO<sub>2</sub> regions around  $30^{\circ}$  N and  $75^{\circ}$  E arrive at the sampling site at Mt. Abu which explained the short duration spikes observed in the measured SO<sub>2</sub> profile against the more broader spikes observed in February 2009. The diurnal pattern observed in the measured  $SO_2$  profile is attributed to the combined effects put in by the insolation dependent variation in the OH radical levels and PBL height as well as the diurnal variation in the wind pattern carrying pollutants to the sampling site from long distances. During this sampling period, three short duration high magnitude spikes were recorded each on 2<sup>nd</sup> (around 0125 hrs) 4<sup>th</sup> (around 2230 hrs) and 5<sup>th</sup> (around 2120 hrs) of Nov '09 which has association with a major oil fire erupted at an IOC depot in Jaipur as the back trajectories showed air parcels reaching the sampling site from co- ordinates surrounding 26.9°N and 75.8°E, during the above days.

During Dec '09, the winds were mostly from North and North-East carrying high SO<sub>2</sub> from the source regions located around co-ordinates  $30^0$  N and  $75^0$  E which resulted in the elevated SO<sub>2</sub> concentration values at the sampling site with many spikes and had a mean and standard deviation recorded of 3.5 ppbv and 1.28 ppbv respectively. A shift in concentration values from higher during the initial sampling days to relatively lower towards the end of the sampling

period is explained by the shift in the wind back trajectories from high  $SO_2$  source regions to low  $SO_2$  regions lying in the eastern side.

The sampling period in Feb '10 saw higher SO<sub>2</sub> values and a clear diurnal variability. High SO<sub>2</sub> values were recorded during the initial sampling period followed by a dip and the concentration again rose towards the end of the sampling period. The observation is well explained by the backward wind trajectories which extended to the high SO<sub>2</sub> regions located around the coordinates  $30^0$  N and  $75^0$  E when high SO<sub>2</sub> values were recorded and the trajectories extended to the west Asian region where no major hot spots of SO<sub>2</sub> are present when dip in SO<sub>2</sub> levels were recorded. The mean SO<sub>2</sub> concentration and the standard deviation recorded during the sampling period are 7.73 ppbv and 1.45 ppbv respectively. The Strong diurnal pattern observed during this sampling period is attributed to the large diurnal PBL height variation.

During the sampling period in Mar '10 also, high SO<sub>2</sub> concentrations were recorded with a mean and standard deviation recorded of 9.19 ppbv and 2.4 ppbv respectively. A well defined diurnal variability pattern is a characteristic feature for this period, which is attributed to the very large diurnal variability in the PBL heights. The diurnal pattern resembled the one observed in Feb '10 with the whole graph shifted by ~ 3 hrs to the left along the time axis which is explained as due to the increase in the insolation rate from February to March at this high altitude site, to cause the PBL height increase to take place in the morning hours itself compared to February. Possible diurnal variation in the wind pattern carrying polluted air to the sampling site also could be another reason for the diurnal SO<sub>2</sub> variability.

The diurnality pattern observed in the measured  $SO_2$  profile over Mt. Abu as well as those in the GEOS-Chem generated  $SO_2$  time series data for different months of the year 2009 can be explained based on the time series PBL height and OH radical values generated using the GEOS-Chem model runs. The GEOS-Chem generated  $SO_2$  profiles showed that during Jan, Feb, Mar, April and May there is a sudden dip in the  $SO_2$  concentration values between 0600 hrs and 0800 hrs IST which is explained on the basis of the diurnality pattern seen in the time series PBL heights as well as OH radical concentration profiles generated using GEOS - Chem. During the above months (Jan, Feb, Mar, April and May), the PBL height remain below 100m during night time till 0600 hrs IST followed by a 10 - 20 fold increase in PBL height by 0800 hrs, which continue to rise till 1400 hrs, remain more or less constant till 1600 hrs, followed by a decrease in its value to reach the minimum value by 2000 hrs IST and continue to remain at this minima till 0600 hrs IST. The diurnal pattern of OH radical for the year 2009 generated using GEOS – Chem showed highest OH radical concentrations during the months, Jun, Jul, Aug, and Sept followed by a decrease till December and then the accenting mode for OH radical levels in the atmosphere start from January. Unlike the diurnality pattern observed for the PBL heights, where during the months of Jan – May there is a transient increase in the values between 0600 hrs and 0800 hrs, the OH variation during the above months are at a relatively slow pace. The sudden increase in OH values between 0600 hrs and 0800 hrs IST takes place during the months May, Jun, July when the relative humidity (RH) in the atmosphere is sufficiently high over this region. The minimum OH radical concentrations were recorded during the month of December when both the insolation as well the atmospheric water content – the two major parameters controlling the OH formation in the atmosphere - are on the lower side.

A study using the GEOS-Chem model, aimed at understanding the possible effects of long range transport on the measured  $SO_2$  values over Mt. Abu showed that there in a decrease in the  $SO_2$  levels in the absence of transport during all the months of the year, but with varying magnitude. The months Jan, Feb, Mar, and April receives the minimum contribution from long range transport while the months July and December sees the highest long range contribution to the ambient  $SO_2$  levels.

The ambient SO<sub>2</sub> measurements over the semi-arid urban site Ahmedabad with numerous industrial establishments and two coal burning thermal power plants in the vicinity were performed during the months, Apr '10, May '10, Jul '10, Aug '10 and Sept '10 to understand the characteristic features of SO<sub>2</sub> spectra over source regions as compared to the remote sites devoid of any local sources.

During April 2010 the SO<sub>2</sub> time series data showed random spikes superimposed on a near constant continuum with a mean SO<sub>2</sub> concentration recorded of 33.13 ppbv and a standard deviation of 22.23 ppbv. Some sort of diurnality pattern was observed for this sampling period, which didn't appear to be to due to the PBL height or OH radical concentration variation but can be attributed to the diurnal variation in the wind pattern carrying polluted air from the nearby thermal power plants and industrial establishments located in the vicinity of few kilometres only. The SO<sub>2</sub> time series recorded during the sampling period in May 2010 showed high concentration values during the initial days of sampling which decreased in magnitude towards the end of the sampling month. The mean and the standard deviation for the sampling period are 26.99 ppbv and 10.76 ppbv respectively with no noticeable diurnality. Similarly, the time-series SO<sub>2</sub> profile obtained during July 2010, which sees the initiation of raining events over the sampling region, recorded a mean SO<sub>2</sub> concentration of 25.63 ppbv and a standard deviation of 5.63 ppbv. The diurnal variability was nil for this month and the spread in the values were near constant during different hours of the day. During Aug 2010 the time series  $SO_2$  profile recorded a mean and standard deviation of 19.15 ppbv and 3.4 ppbv respectively. Similar to the previous month, any observable diurnal variability was absent in this month also. The contribution from long range transport is expected to be a minimum for this month as there are no SO<sub>2</sub> sources below the back trajectories - extending mostly to the Arabian Sea. The sampling period in September 2010 recorded a mean SO<sub>2</sub> concentration and standard deviation of 14.7 ppbv and 2.3 ppbv respectively. No diurnal variability was recorded for this period and the spread in SO<sub>2</sub> values were a minimum. The back trajectories originated in the Arabian Sea and travelled toward the east after reaching the sampling region and hence the long range transported  $SO_2$  is a minimum over the sampling site for this month.

The comparative study, aiming at understanding differences in the formation efficiency of  $SO_4^{2-}$  between sites with different environmental conditions, was undertaken during different months over the two study sites Mt. Abu – a remote high altitude site with occasional long range transport of pollutants - and Shilling – a high rainfall site in North East India. At Mt. Abu

simultaneous measurements of SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> were performed during the months, September '09, October '09, November '09, December '09, February '10 and March '10. The molar ratio of SO<sub>4</sub><sup>2-</sup> to total sulphur compounds (SO<sub>x</sub> = SO<sub>2</sub> + SO<sub>4</sub><sup>2-</sup>) termed molar S-ratio defining the formation efficiency of SO<sub>4</sub><sup>2-</sup> (i.e., the amount of SO<sub>4</sub><sup>2-</sup> produced per SO<sub>2</sub> emitted from the emission sources) was calculated for the above sampling periods for our sampling sites Mt. Abu and Shillong. For this the sulphate (SO<sub>4</sub><sup>2-</sup>) accumulated in the aerosol samples collected during each sampling interval was measured using an ion chromatograph. The median SO<sub>2</sub> concentration during the same sampling interval also was calculated from the 5 min data downloaded from the SO<sub>2</sub> analyzer. Then the average molar S-ratio for that month - a representative of the oxidation efficiency of the atmosphere for the sampling month for that sampling site - is obtained by taking the mean of the molar S-ratio values obtained for each sampling interval.

At Mt. Abu, during the summer months Feb '10 and March '10 the experimentally obtained molar S-ratios were lower compared to the winter months Nov '09 and Dec '09. Intermediate values between these two were recorded during the sampling months Sept '09 and Oct '09, with slightly higher values for the former compared to the latter. The lower S-ratios during the summer months Feb '10 and Mar '10 may be explained by the higher PBL heights compared to the other sampling months and the resulting dilution of SO<sub>2</sub> in the lower layers of the atmosphere to reduce the SO<sub>2</sub> loss from the atmosphere via dry deposition. An increase in the mean free path of the molecules due to higher PBL height - to result in a decrease in the molecular density - also may have resulted in lesser number of collisions between the OH radicals and SO<sub>2</sub> molecules to result in lower conversion efficiencies. Similarly the lower water vapour – a precursor for the OH radical formation in the atmosphere via photo chemistry - content in the atmosphere during the summer months lead to lower concentrations of OH radical resulting in lowering of the atmospheric oxidation efficiency of SO<sub>2</sub>. Lower relative humilities (RH) during the summer months also reduce the chances of heterogeneous phase oxidation on water droplets, lowering the molar S-ratio values further. Even though some of the favourable conditions such as the

relatively higher dust load in the atmosphere exist during these summer months – due to its semi-arid nature – compared to the other sampling months, offering the possibility of heterogeneous phase oxidation on dust surfaces to raise the molar S-ratio values, the effect seems to be insufficient to bring up the molar S-ratio values to the extent that the above discussed negating effects are compensated. Also the possibility of an enhancement in the oxidation efficiency due to longer retention time of SO<sub>2</sub> because of a higher PBL height and the resulting reduced loss due to dry deposition didn't help compensate the molar S-ratio decline. Similarly the possibility of the less contribution from long range transport and hence the absence of aged air masses during these months could be another reason for the observed low molar S-ratio values during Feb '10 and Mar '10.

The PBL heights during the months November and December are among the lowest of the year leading to a higher loss rate of SO<sub>2</sub> to the ground via the dry deposition – as the SO<sub>2</sub> molecular density near the ground are high under low PBL conditions – and hence a high molar S-ratio. the contribution from long range transport to the SO<sub>2</sub> concentration at the sampling site at Mt. Abu is highest during the months November and December, leading to the presence of aged air masses over the sampling site which result in a higher molar S-ratio (But in this case the molar S-ratio needs to be dealt with caution as it is also an indicative of air mass ageing in addition to a measure of the conversion efficiency). The relative humidity also is on the higher side during these months leading to significant contributions from heterogeneous phase oxidation on water droplets to enhance the molar S-ratio values. It appeared that the negative feed-back to the molar S-ratio due to the relatively lower OH radical concentration during these months compared to the rest of the year didn't help pull down the molar S-ratio values.

During the months September and October when the molar S-ratios showed intermediate values lying between the summer months (Feb and March here) and the winter months (Nov and Dec here), it is presumable that the molar S-ratios get both positive and negative feed backs from the parameters such as the PBL height, OH radical concentration, relative humidity and transport of aged air mass. For example during these months, the PBL heights are lower than those for the months of February and March causing a more efficient removal of  $SO_2$  via dry deposition as discussed previously to cause a higher molar S-ratio than these months. Similarly the PBL values for September are less than that for the month of October resulting in more amount of  $SO_2$  getting lost via dry deposition to lead to a higher molar S-ratio for September compared to October. The Relative Humidity for September is higher compared to October to cause higher conversion efficiency and the molar S-ratio, via heterogeneous phase chemistry. Regarding the effect of long range transport, the months September and October sees less  $SO_2$  contribution from long range transport compared to December and hence a lower S-ratio.

A close look at the  $SO_4^{2^-}$  concentration and the median of the  $SO_2$  concentrations recorded in each sampling interval for the sampling period in Sept '09 from which the molar S-ratios were calculated revealed that both  $SO_2$  and  $SO_4^{2^-}$  variations are in phase with each other but with varying magnitudinal difference which is explained as due to a variability in the oxidizing conditions for  $SO_2$  over the sampling site or due to a difference in the source regions for  $SO_2$  from which the long range transport to the sampling site occurred.

In the case of October '09 both  $SO_2$  and  $SO_4^{2-}$  variabilities were in phase during different sampling intervals with the relative difference in the magnitude for  $SO_2$  and  $SO_4^{2-}$  more or less the same throughout the sampling periods indicating the uniformity in the oxidizing conditions prevailing over the sampling site during this month as well as the transport patterns.

During the sampling period in November '09, when a major oil fire erupted at a site located few co-ordinates away from the sampling site at Mt. Abu, the SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> concentrations showed a variability which were in phase during the initial few days of the sampling, slowly started moving out of phase and almost 180 degree out of phase in the second half of the sampling period. This is explained as due to the difference in the transit times of SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> produced during the major oil fire. During the second half of the sampling period the SO<sub>4</sub><sup>2-</sup>

produced over the disaster region via oxidation of the huge amount of SO<sub>2</sub> emitted during the oil fire started reaching the sampling location to give higher  $SO_4^{2-}$ concentrations even when the SO<sub>2</sub> over the sampling location is low. The other possible explanation is that the fire incident ate away a huge amount of OH radicals – the major oxidizing species in the atmosphere – which resulted in reduction in the oxidation efficiency of the atmosphere at least during the night time. The insolation dependent OH radical production cased some OH radical formation during the day time to enhance the SO<sub>2</sub> oxidation process during day time to give the high  $SO_4^{2-}$  values during day time as is the case in the second half of the sampling period.

For the sampling period in December 2009, the  $SO_2$  and  $SO_4^{2-}$  variability showed least correlation in phase and magnitude which is explained as due to the major contribution from long range transport to the measured  $SO_2$  over Mt. Abu compared to the local emissions. When there is relatively higher contribution from long range transport, the  $SO_2$  and  $SO_4^{2-}$  variability may not be expected to be correlating in magnitude and phase, due to the different loss mechanisms and mobility patterns for these two species.

During the sampling period in February 2010, the SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> variations were in phase with each other throughout the sampling period. The observation of a lower magnitude for SO<sub>4</sub><sup>2-</sup> variability compared to SO<sub>2</sub> during the second half of the sampling period is explained on the basis of more favoring oxidizing conditions in the first half compared to the second half of the sampling period. It could also be due to the more contribution from local sources to the measured SO<sub>2</sub> in the second half of the sampling period to result in less aged air mass and hence the lesser conversion. During the sampling period in March 2010, the SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> variations were more or less in phase with each other with few exceptions.

At Shillong the simultaneous measurements of  $SO_2$  and  $SO_4^{2-}$  were made during the months March 2009 and January 2010 and molar S-ratios were calculated. During the sampling period in March 2009, which saw a transient long range transport of  $SO_2$  from high  $SO_2$  source regions in Russia resulting in very high SO<sub>2</sub> concentrations over the sampling site, the molar S-ratio values were very low compared to the molar S-ratios recorded during the sampling period in January 2010. This is explained on the basis of the difference in the mobility as well the loss mechanisms of SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> from the atmosphere. The low molar S-ratios could also be attributed to the low oxidation efficiency of the atmosphere due to the non-availability of sufficient enough OH radicals – the major oxidizing species in the atmosphere – which were almost completely utilized during the initial days of the transport events itself due to the very high SO<sub>2</sub> concentrations in the ambient atmosphere.

For the sampling period in January 2010, which didn't have any major long range contribution, the molar S-ratio values were well within the acceptable limits. A very good correlation is obtained between the  $SO_2$  and  $SO_4^{2-}$  values for different sampling periods in January 2010.

Via extensive use of the GEOS-Chem model, the relative contribution of various parameters such as, OH radical concentration, relative humidity, Planetary Boundary Layer height, dust load in the atmosphere, the dry deposition process, long range transport etc to the molar S-ratio is systematically studied. Similarly the molar S-ratio variation as function of altitude during different seasons of the year also is studied and its possible reasons are explored.

The molar S-ratios calculated using GEOS-Chem for different months of the year 2009 showed a seasonal dependence with the highest values recorded during July and August, and the lowest recorded in the month of April. The trend observed is a steady increase in S-ratio values from April till July; remain steady in August, followed by a decrease till November. The S-ratio values again switch to the accenting mode during December and January followed by a steady descent to reach the lowest value of the year in April.

Both the OH radical concentration as well as the PBL height was found to vary as function of season. In the case of OH radical, the concentrations recorded high values during the months May to September, with the highest value of the year recorded in July. Similarly for different months the PBL heights were found to be systematically varying, recording high values during the months February to June. Since both OH radical as well as PBL height can contribute to the  $SO_2$  seasonal variability, a systematic study is made on the dependence of  $SO_2$  on the OH radical concentration as well as the PBL height for all the months of the year 2009 using GEOS-Chem which showed the varying contribution of PBL height and OH radical concentration in controlling the molar S-ratio during different months.

Similarly, the relative humidity variation as function of season generated using GEOS-Chem for the Indian region showed high values during the months July, Aug, Sept and October. During the times the RH is high the heterogeneous phase oxidation on water droplets is found to play crucial roles in controlling the conversion efficiency of  $SO_2$  in the atmosphere.

To understand the possible effect of heterogeneous phase oxidation on dust surfaces on the Molar S-ratio over the semi-arid site Mt. Abu - characterized by high abundances of mineral dust - GEOS-Chem model runs were performed with Dust emissions turned OFF. In the absence of dust emission, the molar Sratio and hence the SO<sub>2</sub> conversion to SO<sub>4</sub><sup>2-</sup> is decreased below its value for the Full Input run. This underlines the fact that heterogeneous phase oxidation on dust surfaces leads to conversion of more SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> and hence to global cooling.

Similarly to understand the effect of long range transport on the S-ratio over Mt. Abu, GEOS-Chem model runs were performed with Transport Turned OFF in the model. The percent difference in the molar S-ratio when transport is turned OFF showed a seasonal dependence with values oscillating in the positive and negative direction as function of season. During the months Jan, Feb, Mar, April and May, in the absence of transport mechanism the S-ratio enhanced above its value for full input with the highest value recorded in the month of April. Lower values were recorded during the months Jun, July, Aug, Sept and Oct with the lowest value of the year recorded in July. The ascending phase starts from the month of November. Similarly it was found that in the absence of dry deposition, the molar Sratio decreased below its value for Full Input run. This is explained by the known fact that  $SO_2$  is more prone for the physical removal via the dry deposition process compared to  $SO_4^{2^-}$ . The percent difference in S-ratio in the absence of dry deposition is found to be a maximum during the month of August followed by July, underlining the fact that the dry deposition rate is enhanced when clouds are present – as is the case with these high rainfall months. The effect of switching OFF the dry deposition on the molar S-ratio is found to be a minimum during the months March, April and May with the lowest deviation recorded in the month of May. These may be explained by the fact that during these months the boundary layer heights are very high leading to lesser amount of  $SO_2$  and  $SO_4^{2^-}$  in the ground level, to reduce the loss due to the dry deposition process.

#### 6.2. Scope of future research:

The present study though provides significant amount of data on the spatial and seasonal variation in the  $SO_2$  and  $SO_4^{2-}$  concentration over sites with different characteristic features in the Indian region as well as provide an insight into the  $SO_2$  to  $SO_4^{2-}$  conversion efficiency of the atmosphere under varying environmental conditions, the relative contribution of the various atmospheric parameters controlling this conversion efficiency etc., more comprehensive studies can further fine tune the resolution of the results and give better interpretations of the experimental outcomes. A few of them are as follows.

### (a) Size segregated aerosol study:

The sulphate  $(SO_4^{2-})$  measurements from bulk aerosol samples collected during this study provides data on species abundance in an integrated sample of particles present in the atmosphere. Studies based on size-segregated aerosol chemical characteristics would provide information not only about the distribution of the sulphate species in various sizes, but also to better understand the source as well as the physico-chemical transformation processes under varying environmental conditions. Studies using Scanning Electron Microscopy can be highly useful in understanding the morphological features of the sulphate and other aerosol species and thereby better explaining the chemical conversion process of these aerosol species in the atmosphere.

#### (b) Measuring other Gaseous pollutants.

In addition to the ambient  $SO_2$  measurements, a simultaneous monitoring of other pollutant gases directly or indirectly controlling the OH radical concentration and hence the  $SO_2$  conversion efficiency can better explain the observed variations in the molar S-ratio under various atmospheric conditions. For example pollutant gases such as  $NO_x$  and CO can eat away significant amount of OH radicals under high pollution events leading to the low oxidation efficiency of the atmosphere. Similarly the concentration of Ozone and water vapour are important parameters controlling the OH radical concentration in the atmosphere and a simultaneous monitoring of them is very essential to better understand the molar S-ratios.

### (c) EC and OC measurements

It is known that the Elemental Carbon (EC) as well as Organic Carbon (OC) contribute to a significant fraction of the total aerosol mass and influence the climate via radiative forcing and through its effects on the hydrological cycle. A systematic direct measurement of EC and OC in the aerosol samples can better explain the contribution of heterogeneous phase oxidation on these aerosols to the molar S-ratio values.

- Adams, P. J., et al. (2001), General circulation model assessment of direct radiative forcing by the sulfate-nitrate-ammonium-water inorganic aerosol system, J. Geophys. Res., 106(D1), 1097-1111.
- Andreae, M. O., et al. (1988), Vertical distribution of dimethylsulfide, sulfur dioxide, aerosol ions, and radon over the northest pacific Ocean, J. Atmos. Chem., 6 (1-2), 149-173.
- Andreae, M. O. (1990), Ocean-atmosphere interactions in the global biogeochemical sulfur cycle, *Mar. Chem*, 30, 1-29.
- Andreae, M. O., and W. A. Jaeschke (1992), Exchange of sulfur between biosphere and atmosphere over temperate and tropical regions, in *Sulfur Cycling in Terrestrial Systems and Wetlands*, edited by R. W. Howarth and J. W. B. Stewart, John Wiley, New York.
- Andreae, M. O., and P. J. Crutzen (1997), Atmospheric Aerosols: Biogeochemical Sources and Role in Atmospheric Chemistry, *Science*, 276(5315), 1052-1058.
- Atkinson, R. (1997), Gas-phase tropospheric chemistry of volatile organic compounds, 1, Alkanes and alkenes, J. Phys. Chem. Ref. Data, , 26, 215-290.
- Bailey, R., et al. (2000), Atmospheric organochlorine pesticides in the western Canadian Arctic: Evidence of transpacific transport, J. Geophys. Res., 105(D9), 11805-11811.
- Bates, T. S., et al. (1987), Regional and seasonal variations in the flux of oceanic dimethyl sulfide to the atmosphere, *J. Geophys. Res.*, *92*, 2930-2938.
- Benkovitz, C. M., et al. (1996), Global gridded inventories of anthropogenic emissions of sulfur and nitrogen, J. Geophys. Res., 101(D22), 29239-29253.
- Bey, I., et al. (2001), Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation, J. Geophys. Res., 106(D19), 23073-23095.
- Bhattacharya, A. B., et al. (1996), Diffuse solar radiation and associated meteorological parameters in India, *Annales Geophysicae*, *14*(1051-1059).

- Boucher, O., and M. Pham (2002), History of sulfate aerosol radiative forcings, *Geophys. Res. Lett.*, 29(9), 1308.
- Breon, F. M., et al. (2002), Aerosol effect on cloud droplet size monitored from satellite, *Science*, 295, 834-838.
- Brown, S. S., et al. (1999a), Rate constant for the reaction OH+NO<sub>2</sub> + M --> HNO<sub>3</sub>+M under atmospheric conditions, *Chem. Phys. Lett.*, 299, 277-284.
- Brown, S. S., et al. (1999b), Reconsideration of the rate constants for the reaction of hydroxyl radicals with nitric vapor, *J. Phys. Chem.*, *103*, 3031-3037.
- Chameides, W. L. e. a. (1999), Case study of the effects of atmospheric aerosols and regional haze on agriculture: An opportunity to enhance crop yields in China through emission controls?, in *Proc. Natl. Acad. Sci.*, edited, pp. 13,626-613,633, U. S. A.
- Chaudhry, Z., et al. (2007), In situ measurements of aerosol mass concentration and radiative properties in Xianghe, southeast of Beijing, *J. Geophys. Res.*, *112*(D23), D23S90.
- Chaudhry, Z. (2008), A study of optical, physical, and chemical properties of aerosols using in situ measurement, Ph. D. dissertation, College Park.
- Chen, D., et al. (2009), Regional CO pollution and export in China simulated by the highresolution nested-grid GEOS-Chem model, *Atmos. Chem. Phys.*, 9(11), 3825-3839.
- Cheng, Y. F., et al. (2009), Influence of soot mixing state on aerosol light absorption and single scattering albedo during air mass aging at a polluted regional site in northeastern China, *J. Geophys. Res.*, *114*(D2), D00G10.
- Clarke, A. D., et al. (2001), Dust and pollution transport on global scales: Aerosol measurements and model predictions, *J. Geophys. Res.*, *106*(D23), 32555-32569.
- Cullis, C. F., and M. M. Hirschler (1980), Atmospheric sulphur: Natural and man-made sources, *Atmospheric Environment* (1967), 14(11), 1263-1278.
- DeMore, W. B., et al. (1997), Chemical kinetics and photochemical data for use in stratospheric modeling, *JPL Publ*, 97-4, 1-278.
- Dentener, F. J., et al. (1996), Role of mineral aerosol as a reactive surface in the global troposphere, *J. Geophys. Res.*, *101*(D17), 22869-22889.

- Draxler, R. R., and G. D. Rolph (2003), HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (<u>http://www.arl.noaa.gov/ready/hysplit4.html</u>), NOAA Air Resources Laboratory, Silver Spring, MD.
- Duce, R. A., et al. (1980), Long-range atmospheric transport of soil dust from Asia to the tropical North Pacific: Temporal Variability, *Science*, 209, 1522-1524.
- Duncan Fairlie, T., et al. (2007), The impact of transpacific transport of mineral dust in the United States, *Atmospheric Environment*, *41*(6), 1251-1266.
- Freney, J. R., et al. (1983), The sulphur cycle, in The Major Biogeochemical Cycles and Their Interactions, SCOPE 24, edited by B. Bolin and C. R. B, pp. 56-61, John Wiley, New York.
- Fu, T.-M., et al. (2007), Space-based formaldehyde measurements as constraints on volatile organic compound emissions in east and south Asia and implications for ozone, J. Geophys. Res., 112(D6), D06312.
- Fu, T.-M., et al. (2008), Global budgets of atmospheric glyoxal and methylglyoxal, and implications for formation of secondary organic aerosols, J. Geophys. Res., 113(D15), D15303.
- Gassó, S. (2008), Satellite observations of the impact of weak volcanic activity on marine clouds, *J. Geophys. Res.*, *113*(D14), D14S19.
- Gerhardsson, L., et al. (1994), Acid precipitation -- effects on trace elements and human health, *The Science of The Total Environment*, *153*(3), 237-245.
- Guenther, A., et al. (2006), Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), Atmos. Chem. Phys., 6(11), 3181-3210.
- Guttikunda, S. K., et al. (2003), The contribution of megacities to regional sulfur pollution in Asia, *Atmospheric Environment*, *37*(1), 11-22.
- Harris, J. M., et al. (1992), Variations in Atmospheric Methane at Mauna Loa Observatory Related to Long-Range Transport, J. Geophys. Res., 97(D5), 6003-6010.
- Haywood, J., and O. Boucher (2000), Estimates of the direct and indirect radiative forcing due to tropospheric aerosols: A review, *Rev. Geophys.*, *38*(4), 513-543.

- Hidy, G. M., et al. (1978), Spatial and temporal distributions of airborne sulfate in parts of the United States, *Atmospheric Environment* (1967), 12(1-3), 735-752.
- Hoell, J. M., et al. (1997), The Pacific Exploratory Mission-West Phase B: February-March, 1994, J. Geophys. Res., 102(D23), 28223-28239.
- Höller, R., et al. (2003), Wavelength-dependent aerosol single-scattering albedo: Measurements and model calculations for a coastal site near the Sea of Japan during ACE-Asia, J. Geophys. Res., 108(D23), 8648.
- Horowitz, L. W., et al. (1998), Export of reactive nitrogen from North America during summertime: Sensitivity to hydrocarbon chemistry, J. Geophys. Res., 103(D11), 13451-13476.
- Hudman, R. C., et al. (2007), Surface and lightning sources of nitrogen oxides over the United States: Magnitudes, chemical evolution, and outflow, J. Geophys. Res., 112(D12), D12S05.
- Husar, R. B., and D. E. Patterson (1980), Regional scale air pollution sources and effects, 241-247 pp, Ann. N.Y. Acad. Sci.
- Igarashi, Y., et al. (2004), Monitoring the SO2 concentration at the summit of Mt. Fuji and a comparison with other trace gases during winter, *J. Geophys. Res.*, *109*(D17), D17304.
- IPCC (2007), Intergovernmental Panel on Climate Change, Report
- Jacobson, M. Z., and R. P. Turco (1994), A sparse-matrix, vectorized GEAR code for atmospheric transport models, *Atmospheric Environment*, *33*, 273-284.
- Jaffe, D., et al. (1999), Transport of Asian air pollution to North America, *Geophys. Res.* Lett., 26(6), 711-714.
- Jaffe, D., et al. (2003a), Six 'new' episodes of trans-Pacific transport of air pollutants, *Atmos. Environ.*, 37, 391-404.
- Jaffe, D., et al. (2003b), Increasing background ozone during spring on the west coast of North America, *Geophys. Res. Lett.*, *30*(12), 1613.
- Kaneyasu, N., et al. (1995), Seasonal variation in the chemical composition of atmospheric aerosols and gaseous species in Sapporo, Japan, Atmospheric Environment, 29(13), 1559-1568.

- Krishnan, P., and P. K. Kunhikrishnan (2004), Temporal variations of ventilation coefficient at a tropical Indian station using UHF wind profiler, *Current Science*, 86(447-450).
- Krueger, B. J., et al. (2003), The transformation of solid atmospheric particles into liquid droplets through heterogeneous chemistry: Laboratory insights into the processing of calcium containing mineral dust aerosol in the troposphere, *Geophys. Res. Lett.*, 30(3), 1148.
- Kuhns, H., et al. (2003), Big Bend Regional Aerosol and Visibility Observational (BRAVO) study emissions inventory Desert Res. Inst., Las Vegas, Nev.
- Kulmala, M., et al. (2004), Formation and growth rates of ultrafine atmospheric particles: a review of observations, *Journal of Aerosol Science*, *35*(2), 143-176.
- Lee, C., et al. (2009), Retrieval of vertical columns of sulfur dioxide from SCIAMACHY and OMI: Air mass factor algorithm development, validation, and error analysis, *J. Geophys. Res.*, 114(D22), D22303.
- Leung, F.-Y. T., et al. (2007), Impacts of enhanced biomass burning in the boreal forests in 1998 on tropospheric chemistry and the sensitivity of model results to the injection height of emissions, *J. Geophys. Res.*, *112*(D10), D10313.
- Li, X., and W. Song (2009), DUST STORM DETECTION BASED ON MODIS DATA paper presented at International Conference on Geo-spatial Solutions for Emergency Management and the 50th Anniversary of the Chinese Academy of Surveying and Mapping Chinese Academy of Surveying and Mapping No.16 Beitaiping, Haidian District, Beijing, P.R.China (100039) Beijing, China 14-16 September 2009
- Li, Z. (2004), Aerosol and climate: A perspective from East Asia, in Observation, Theory, and Modeling of the Atmospheric Variabillity, in World Sci., edited, pp. 501-525, Hackensack, N. J.
- Li, Z., et al. (2007), Preface to special section on East Asian Studies of Tropospheric Aerosols: An International Regional Experiment (EAST-AIRE), *J. Geophys. Res.*, *112*(D22), D22S00.
- Liu, T. S. (1985), Loess and the Environment, China Ocean, Beijing, 251 pp.

- Luke, W. T. (1997), Evaluation of a commercial pulsed fluorescence detector for the measurement of low-level SO2 concentrations during the Gas-Phase Sulfur Intercomparison Experiment, J. Geophys. Res., 102(D13), 16255-16265.
- Luria, M., et al. (1992), ATMOSPHERIC SULFUR DIOXIDE AT MAUNA LOA, HAWAII, J. Geophys. Res., 97(D5), 6011-6022.
- Maahs, H. G. (1983), Kinetics and Mechanism of the Oxidation of S(IV) by Ozone in Aqueous Solution With Particular Reference to SO2 Conversion in Nonurban Tropospheric Clouds, *J. Geophys. Res.*, 88(C15), 10721-10732.
- Martin, R. V. (2008), Satellite remote sensing of surface air quality, Atmospheric Environment, 42, 7823-7843.
- Merril, J. T., et al. Meteorological analysis of long-range transport of mineral aerosols over the North Pacific, *J. Geophys. Res.*, *94*, 8584-8598.
- Millet, D. B., et al. (2008), Spatial distribution of isoprene emissions from North America derived from formaldehyde column measurements by the OMI satellite sensor, J. Geophys. Res., 113(D2), D02307.
- Miyakawa, T., et al. (2007), Removal of sulfur dioxide and formation of sulfate aerosol in Tokyo, *J. Geophys. Res.*, *112*(D13), D13209.
- Monn, C., and G. Schaeppi (1993), Concentrations of total suspended particulates, fine particles and their anionic compounds in ambient air and Indoor air, *Environmental Technology*, *14*(9), 869 875.
- Moore, K. G., II, et al. (2003), Long-range transport of continental plumes over the Pacific Basin: Aerosol physiochemistry and optical properties during PEM-Tropics A and B, *J. Geophys. Res.*, *108*(D2), 8236.
- Olivier, J. G. J., and J. J. M. Berdowski (2001), Global emissions sources and sinks, in The Climate System A.A. Balkema Publishers/Swets & Zeitlinger Publishers Lisse, The Netherlands
- Park, R. J., et al. (2004), Natural and transboundary pollution influences on sulfatenitrate-ammonium aerosols in the United States: Implications for policy, J. Geophys. Res., 109(D15), D15204.
- Perry, K. D., et al. (1999), Long-range transport of anthropogenic aerosols to the National Oceanic and Atmospheric Administration baseline station at Mauna Loa Observatory, Hawaii, J. Geophys. Res., 104(D15), 18521-18533.

- Pham, M., et al. (2005), Changes in atmospheric sulfur burdens and concentrations and resulting radiative forcings under IPCC SRES emission scenarios for 1990–2100, J. Geophys. Res., 110(D6), D06112.
- Prospero, J. M., et al. (2003), Long-term record of nss-sulfate and nitrate in aerosols on Midway Island, 1981–2000: Evidence of increased (now decreasing?) anthropogenic emissions from Asia, J. Geophys. Res., 108(D1), 4019.
- Qian, Y., et al. (2006), More frequent cloud-free sky and less surface solar radiation in China from 1955 to 2000, *Geophys. Res. Lett.*, *33*(1), L01812.
- Ramachandran, S., and S. Kedia Black carbon aerosols over an urban region: Radiative forcing and climate impact, *J. Geophys. Res.*, *115*(D10), D10202.
- Ramaswamy, V., et al. (2001), Radiative forcing of climate change. In: Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change, edited by J. T. Houghton, et al., pp. 349-416, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- Rastigejev, Y., et al. Resolving intercontinental pollution plumes in global models of atmospheric transport, J. Geophys. Res., 115(D2), D02302.
- Rastogi, N., and M. M. Sarin (2005), Long-term characterization of ionic species in aerosols from urban and high-altitude sites in western India: Role of mineral dust and anthropogenic sources, *Atmospheric Environment*, *39*(30), 5541-5554.
- Rastogi, N., and M. M. Sarin (2006), Chemistry of aerosols over a semi-arid region: Evidence for acid neutralization by mineral dust, *Geophys. Res. Lett.*, 33(23), L23815.
- Rengarajan, R., and M. M. Sarin (2004), Atmospheric deposition fluxes of <sup>7</sup>Be, <sup>210</sup>Pb and chemical species to the Arabian Sea and Bay Bengal, *Ind. J. Mar. Sci.*, *33*, 56-64.
- Rodhe, H., and I. Isaksen (1980), Global distribution of sulfur compounds in the troposphere estimated in a height/latitude transport model, *J. Geophys. Res.*, 85, 7401-7409.
- Rolph, G. D. (2003), Real-time Environmental Applications and Display System (READY), NOAA Air Resour. Lab., Silver Spring, Md. (Available as <u>http://www.arl.noaa.gov/ready/hysplit4.html)</u>.

- Saltzman, E. S., and C. D. J. (1988), Shipboard measurements of atmospheric dimethyl sulfide and hydrogen sulfide in the Caribbean and Gulf of Mexico, *J. Atmos. Chem.*, 7, 191-209.
- Sander, S. P., and J. H. Seinfeld (1976), Chemical kinetics of homogeneous atmospheric oxidation of sulfur dioxide, *Environmental Science & Technology*, 10(12), 1114-1123.
- SCHINDLER, D. W. (1988), Effects of Acid Rain on Freshwater Ecosystems, *Science*, 239(4836), 149-157.
- Seinfeld, J. H., and S. N. Pandis (1998), Atmospheric Chemistry and Physics, edited by J.H. Seinfeld, Pandis, S. N., Wiley-Interscience, Hoboken, N. J.
- Selin, N. E., and D. J. Jacob (2008), Seasonal and spatial patterns of mercury wet deposition in the United States: Constraints on the contribution from North American anthropogenic sources, *Atmospheric Environment*, 42, 5193-5204.
- Sharma, A. R., et al. (2010), An Unusual Dust Event over North-eastern India and its Association with Extreme Climatic Conditions- A Study Using Satellite Data, paper presented at IASTA-2010, Conference of Indian Aerosol Science & Technology Association on AEROSOLS & CLOUDS: CLIMATE CHANGE PERSPECTIVES, Bose Institute, Darjeeling Campus, March 24-26, 2010.
- Shaw, G. (1980), Transport of Asian desert aerosol to the Hawaiian Islands, J. Appl. Meteorol., 19, 1254-1259.
- Shim, C., et al. (2008), Evaluation of model-simulated source contributions to tropospheric ozone with aircraft observations in the factor-projected space, *Atmos. Chem. Phys.*, 8, 1751-1761.
- Smith, S. J., et al. (2004), Historical Sulphur Dioxide Emissions 1850-2000: Methods and Results.
- Solomon, S., et al. (2007), Technical summary, in *Climate Change 2007: The Physical* Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change.
- Spiro, P. A., et al. (1992), Global Inventory of Sulfur Emissions With 1°×1° Resolution, J. Geophys. Res., 97(D5), 6023-6036.

- Spracklen, D. V., et al. (2009), Impacts of climate change from 2000 to 2050 on wildfire activity and carbonaceous aerosol concentrations in the western United States, J. Geophys. Res., 114(D20), D20301.
- Steding, D. J., and A. R. Flegal (2002), Mercury concentrations in coastal California precipitation: Evidence of local and trans-Pacific fluxes of mercury to North America, J. Geophys. Res., 107(D24), 4764.
- Streets, D. G., et al. (2006), Revisiting China's CO emissions after the Transport and Chemical Evolution over the Pacific (TRACE-P) mission: Synthesis of inventories, atmospheric modeling, and observations, J. Geophys. Res., 111(D14), D14306.
- Sun, J., et al. (2001), Spatial and temporal characteristics of dust storms in China and its surrounding regions, 1960–1999: Relations to source area and climate, J. Geophys. Res., 106(D10), 10325-10333.
- Suntharalingam, P., et al. (2008), Global 3-D model analysis of the seasonal cycle of atmospheric carbonyl sulfide: Implications for terrestrial vegetation uptake, *Geophys. Res. Lett.*, 35(19), L19801.
- Takemura, T., et al. (2005), Simulation of climate response to aerosol direct and indirect effects with aerosol transport-radiation model, J. Geophys. Res., 110(D2), D02202.
- Thornton, D. C., et al. (1996), Sulfur dioxide as a source of condensation nuclei in the upper troposphere of the Pacific Ocean, *J. Geophys. Res.*, *101*(D1), 1883-1890.
- Thornton, D. C., et al. (1997), Transport of sulfur dioxide from the Asian Pacific Rim to the North Pacific troposphere, *J. Geophys. Res.*, *102*(D23), 28489-28499.
- Toon, O. B., et al. (1987), The sulfur cycle in the marine atmosphere, *J. Geophys. Res.*, 92, 943-963.
- Vestreng, V., and H. Klein (2002), Emission data reported to UNECE/EMEP. Quality assurance and trend analysis and Presentation of WebDab, MSC-W Status Report 2002 Norwegian Meteorological Institute, Oslo, Norway
- Wang, J., et al. (2008), Sensitivity of sulfate direct climate forcing to the hysteresis of particle phase transitions, J. Geophys. Res., 113(D11), D11207.
- Wang, Y., et al. (2007), Assessing the photochemical impact of snow NOx emissions over Antarctica during ANTCI 2003, *Atmospheric Environment*, 41, 3944-3958.

- Wesely, M. L. (1989), Parameterization of surface resistance to gaseous dry deposition in regional-scale numerical models, *Atmos. Environ.*, 23, 1293-1304.
- Wild, O., et al. (2000), Accurate simulation of in- and below- cloud photolysis in global chemical models, J. Atmos. Chem., 37, 245-282, *J. Atmos. Chem.*, 37, 245-282.
- Wilkening, K. E., et al. (2000), Atmospheric Science: Trans-Pacific air pollution, *Science*, 290, 65-67.
- Wu, S., et al. (2008), Effects of 2000–2050 global change on ozone air quality in the United States, J. Geophys. Res., 113(D6), D06302.
- Wu, S., et al. (2009), Chemical nonlinearities in relating intercontinental ozone pollution to anthropogenic emissions, *Geophys. Res. Lett.*, 36(5), L05806.
- Xiao, H., et al. (1997), Long-range transport of SO x and dust in East Asia during the PEM B Experiment, *J. Geophys. Res.*, *102*(D23), 28589-28612.
- Xiao, Y., et al. (2008), Global budget of ethane and regional constraints on U.S. sources, J. Geophys. Res., 113(D21), D21306.
- Xu, M., et al. (2006), Steady decline of east Asian monsoon winds, 1969–2000:
  Evidence from direct ground measurements of wind speed, J. Geophys. Res., 111(D24), D24111.
- Xu, Q. (2001), Abruput change of the mid-summer climate in central east China by the influence of atmospheric pollution, *Atmos. Environ*.(35), 5029-5040.
- Yu, F., et al. (2007), Ion-mediated nucleation as an important global source of tropospheric aerosols Atmos. Chem. Phys. Discuss, 7, 13597-13626.
- Yu, H., et al. (2002), Radiative effects of aerosols on the evolution of the atmospheric boundary layer, J. Geophys. Res., 107(D12), 4142.
- Zhang, L., et al. (2009), Intercontinental source attribution of ozone pollution at westernU.S. sites using an adjoint method, *Geophys. Res. Lett.*, 36(11), L11810.
- Zhang, L., et al. (2010), Impact of the Southeast Asian summer monsoon strength on the outflow of aerosols from South Asia, Ann. Geophys., 28, 277–287.

List of Publications:

Published: (In Peer-reviewed Journals)

- Timmy Francis (2011), "Effect of Asian Dust Storms on the Ambient SO<sub>2</sub> Concentration over North-East India: A Case Study", J. Environmental Protection 2011, 2, 778-795, doi:10.4236/jep.2011.26090
- A. K. Singhvi, M. A. J. Williams, S. N. Rajaguru, V. N. Misra, S. Chawla, S. Stokes, N. Chauhan, T. Francis, R. K. Ganjoo and G. S. Humphreys, (2010), "A ~200 ka record of climatic change and dune activity in the Thar Desert, India", Quaternary Sci. Revs, Volume 29, Issues 23-24, Pages 3095-3105, doi:10.1016/j.quascirev.2010.08.003

# Manuscripts under Preparation:

- Timmy Francis and M. M. Sarin, "Spatio-temporal trends in the Sulphur conversion efficiency of the Atmosphere: Model versus Observations" (to be submitted to J. Geophysical Res- Atmosphere)
- 2) Timmy Francis and M. M. Sarin, "*Temporal trends in the ambient SO*<sub>2</sub> *Conc. over a high altitude Semi-arid site in India: Photo-Chemistry and other models*"(to be submitted to Atmos. Environment)
- **3) Timmy Francis** and M. M. Sarin, "Suppression of the oxidation efficiency of the atmosphere during a major plume transport event"(to be submitted to J. Atmospheric Chemistry)
- 4) **Timmy Francis** and M. M. Sarin, "Ambient SO<sub>2</sub> concentration over a semi-arid urban site in Western India: Seasonal trends" (to be submitted to J. Environmental Protection)

# Abstracts (Conference/Symposia)

- Timmy Francis and Manmohan Sarin, "Atmospheric SO<sub>2</sub> concentrations over highdust region in western India: Temporal variability and transformation to SO<sub>4</sub><sup>2-</sup>", P-Observations 2.91, ID: 4274, ICACGP-IGAC-2010, July 11-16, 2010, Halifax, Canada.
- Timmy Francis and M. M. Sarin, "Spatio-temporal variability in the atmospheric conversion efficiency of sulphur dioxide to sulphate" 16<sup>th</sup> National Space Science Symposium (NSSS – 2010) of the Indian Space Research Organization (ISRO), February 24-27, 2010, Saurashtra University, Rajkot, India.